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THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF FOUR SPIN SYSTEMS

II.[1] Proton Resonance Spectra of Some *Para*-Disubstituted Benzenes

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ABSTRACT

The spectra of a number of *p*-disubstituted benzenes were analyzed earlier by Richards and Schaeffer by assuming that the two *meta* H–H coupling constants are equal and the *para* H–H coupling constant is zero. In the present work a method for analysing this type of spectra, without making any simplifying assumptions, is proposed. The proton resonance spectra of *p*-bromochlorobenzene, *p*-chlorotoluene and *p*-chloroiodobenzene were obtained and analyzed as examples, and all the parameters were determined in each case. The general form of this type of spectra for different values of chemical shift is discussed.

1. INTRODUCTION

THE general theory of the spectra of four spin systems, which can be divided into two pairs of two equivalent nuclei (A_2B_2 type), was discussed by Pople, Bernstein and Schneider.[1, 2] There are twenty-eight transitions in the spectrum out of which four are combination transitions of feeble intensity. The remaining twenty-four transitions occur symmetrically about the centre of the spectrum and therefore the analysis can be completely done if the twelve transitions in a typical half of the spectrum are identified. Explicit expressions in terms of the involved parameters (one chemical shift and four spin-spin coupling constants) can be derived for only six of these twelve transitions, and the spectrum depends on the chemical shift and the spin-spin coupling constants in a rather complicated manner. A straightforward analysis is therefore not usually possible. Pople *et al.*,[1, 2] however, proposed some practical methods of analysis for some special cases of this type of spectra (*a*) when the two AB coupling constants are equal and (*b*) when one pair of nuclei are more strongly coupled than the other.

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[1] Our earlier paper on "H^1 and F^{19} Resonance Spectra of 1-fluoro, 2, 4-dinitrobenzene," *Proc. Ind. Acad. Sci.*, 1960, **52 A**, 109, is referred to as I.

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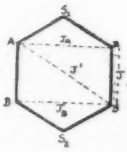
The proton resonance spectra of *p*-disubstituted benzenes (where the substituents do not interfere in the spectrum) belong to a different case of A_2B_2 spectra as the nuclei in each pair are strongly coupled to nearly the same extent. Richards and Schaeffer[3] (hereafter referred to as RS) have recently studied the spectra of a number of these compounds at 29·92 mc./sec., and carried out the analysis by making the simplifying assumptions that the coupling constants J_A and J_B are equal and that $J' = 0$ (*see* Fig. 1). As shown later in this paper there is no pressing necessity, however, to make these assumptions.



S_1 and S_2 are the substituents

FIG. 1.

We have here studied again the proton resonance spectra of three *p*-disubstituted benzenes at 40 mc./sec. A general method for analyzing this type of spectra is proposed, and on this basis all the parameters were obtained in each case.

2. EXPERIMENTAL

All the three compounds studied, *viz.*, *p*-bromochlorobenzene, *p*-chlorotoluene and *p*-chloroiodobenzene were obtained from British Drug House and were used without further purification. *p*-chlorotoluene is a liquid and the other two compounds are solids. For *p*-bromochlorobenzene a solution in ether and for *p*-chloroiodobenzene a solution in ethanol were used.*

The spectra were all obtained on a Varian V-4300 B High Resolution N.M.R. Spectrometer. The general experimental details for the proton resonance studies at 40 mc./sec. were given in I[4]. The observed line frequencies are all expressed with respect to the centre of the spectrum to facilitate comparison with the theoretical spectrum (*see* Table III).

The experimental spectra of *p*-bromochlorobenzene, *p*-chlorotoluene and *p*-chloroiodobenzene are reproduced in Figs. 2 (*a*), 3 (*a*) and 4 (*a*) respectively.

3. METHOD OF ANALYSIS

The complete spin matrix for the A_2B_2 system and the explicit expressions for the energy levels and the corresponding wave functions, and the

* The solvents are the same as those used by RS for these compounds.

transition energies and relative intensities in cases where these can be derived, were given by Pople *et al.*[1, 2] The notation employed by them is freely used throughout this paper without specification. The calculations can be conveniently done in terms of new quantities K, L, M and N defined as below:

$$\left.\begin{aligned} K &= J_A + J_B & N &= J + J' \\ M &= J_A - J_B & L &= J - J' \end{aligned}\right\}. \tag{1}$$

Explicit expressions were derived for all but four of the energy levels which were labelled as $1s_0'$, $2s_0'$, $3s_0'$ and $4s_0'$. If we denote the energy values corresponding to these four states as E_1, E_2, E_3 and E_4 respectively, these are given by the roots of the fourth power equation (obtained by expanding the corresponding 4×4 determinant):

$$\begin{aligned}(K+E)\{E^3 + NE^2 - E[\tfrac{1}{4}N^2 + (\nu_0\delta)^2] - \tfrac{1}{4}N^3\} \\ - \tfrac{1}{4}L^2\{3E^2 - [\tfrac{1}{4}N^2 + (\nu_0\delta)^2]\} = 0\end{aligned} \tag{2}$$

where $\nu_0\delta$ is the chemical shift in cps.

The exact eigenfunctions ϕ_q $(q = 1, \ldots, 4)$ for these four levels can be expressed as linear combinations of the zero order wave functions $\phi^0{}_m$ $(m = 1, \ldots, 4)$ of the four states, *i.e.*,

$$\phi_q = \sum_m a_{qm}\phi^0{}_m \tag{3}$$

where the coefficients a_{qm} may be evaluated in the usual manner[2, 5] if the parameters are determined.

Six of the twelve 'A' (or 'B') transitions involve these energy levels and the energies of these transitions may tentatively be expressed in terms of E_1, E_2, E_3 and E_4. The relative intensities may also be calculated in terms of the coefficients a_{qm} in Eq. (3). The transition energies and relative intensities of all the twelve transitions are given, in this manner, in Table I.

To proceed with the analysis, taking a typical half of the spectrum, the lines 1 and 3 (line Nos. as in Table I) may first be identified. The identification is easier if an approximate value of N is known, as the separation between the lines is N.* If these lines are fixed, at least tentatively, $\nu_0\delta$ and N can easily be obtained.

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* In the case of *p*-disubstituted benzenes N is equal to the sum of the *ortho* and *para* H–H coupling constants and its value may be expected to be about 9·0 cps., from the known data on these constants in other compounds. It is reasonable to expect like this as the coupling constants are not, in general, found to be much sensitive to substitution.

TABLE I*

Transition energies and relative intensities for the 'A' spectrum

Sl. No.	Transition	Energy relative to $\frac{1}{2}(\nu_A+\nu_B)$	Relative intensity
1	$1s_1' \rightarrow s_2$	$\frac{1}{2}N+\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}$	$1-\sin 2\phi$
2	$1s_0' \rightarrow 1s_1'$	$-\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}-E_1$	$[\cos\phi\,(a_{11}+a_{14})-\sin\phi \times(a_{12}+a_{14})]^2$
3	$s_{-2} \rightarrow 1s_{-1}'$	$-\frac{1}{2}N+\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}$	$1+\sin 2\phi$
4	$1s_{-1}' \rightarrow 2s_0'$	$E_2-\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}$	$[\cos\phi\,(a_{22}+a_{24})+\sin\phi \times(a_{21}+a_{24})]^2$
5	$3s_0' \rightarrow 2s_1'$	$\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}-E_3$	$[\cos\phi\,(a_{32}+a_{34})+\sin\phi \times(a_{31}+a_{34})]^2$
6	$2s_{-1}' \rightarrow 4s_0'$	$E_4+\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}$	$[\cos\phi\,(a_{41}+a_{44})-\sin\phi \times(a_{42}+a_{44})]^2$
7	$4s_0' \rightarrow 2s_1'$	$\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}-E_4$	$[\cos\phi\,(a_{42}+a_{44})+\sin\phi \times(a_{41}+a_{44})]^2$
8	$2s_{-1}' \rightarrow 3s_0'$	$E_3+\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}$	$[\cos\phi\,(a_{31}+a_{34})-\sin\phi \times(a_{32}+a_{34})]^2$
9	$2a_0' \rightarrow 2a_1'$	$\frac{1}{2}[(\nu_0\delta+M)^2+L^2]^{\frac{1}{2}} + \frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a-\psi_+)$
10	$2a_{-1}' \rightarrow 1a_0'$	$\frac{1}{2}[(\nu_0\delta-M)^2+L^2]^{\frac{1}{2}} + \frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a+\psi_-)$
11	$1a_0' \rightarrow 2a_1'$	$\frac{1}{2}[(\nu_0\delta+M)^2+L^2]^{\frac{1}{2}} - \frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a-\psi_+)$
12	$2a_{-1}' \rightarrow 2a_0'$	$\frac{1}{2}[(\nu_0\delta-M)^2+L^2]^{\frac{1}{2}} - \frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a+f\psi_-)$

* The expressions for transitions 1, 3, 9, 10, 11 and 12 are the same as those on p. 144 of reference 2.

In molecules like the *p*-disubstituted benzenes one might expect the value of M to be small, and N and L to be nearly equal. Then the lines 9 and 10 will lie close to 1, and lines 11 and 12 will lie close to 3. Sometimes these lines (9–12) may not be separated sufficiently from lines 1 and 3 to be observed. These transitions may therefore be considered towards the end of the analysis.

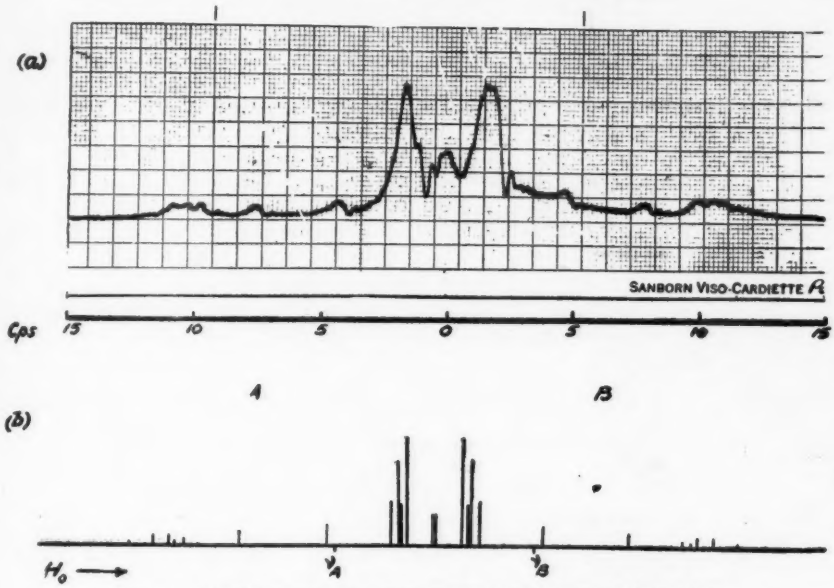

FIG. 2. H^1 NMR spectrum of *para*-bromochlorobenzene at 40 mc./sec.
(*a*) Experimental, (*b*) Calculated: 1 cm. = 1·936 Cps.

We will now be left with the six transitions 2, 4, 5, 6, 7 and 8, and these involve the roots of the Eq. (2), in which the quantities K and L^2 are yet to be determined ($\nu_0\delta$ and N are already known from the identification of the lines 1 and 3). From Table I it can be seen that the sum of the transition frequencies of 5 and 8 as well as that of 6 and 7 are both equal to $[(\nu_0\delta)^2 + N^2]^{\frac{1}{2}}$. The value of this factor is known, and therefore we can pick up from the rest of the lines in the observed spectrum, two pairs of lines such that the sum of the frequencies of the lines, with respect to $\frac{1}{2}(\nu_A + \nu_B)$, in each pair is equal to $[(\nu_0\delta)^2 + N^2]^{\frac{1}{2}}$. If the frequencies of these lines are say ν_5 & ν_8, and ν_6 & ν_7 we find that

$$E_3 = \pm\frac{\nu_5 - \nu_8}{2} \quad \text{and} \quad E_4 = \pm\frac{\nu_6 - \nu_7}{2}. \tag{4}$$

From this identification we therefore get two probable values of E_3 and two for E_4, out of which one is to be discarded in each case. If we substitute these four roots of E in Eq. (2), we get four equations each involving K and L.[2]

As mentioned earlier we know that the values of N and L are close to each other, as the *para* H–H coupling constant is expected to be small,

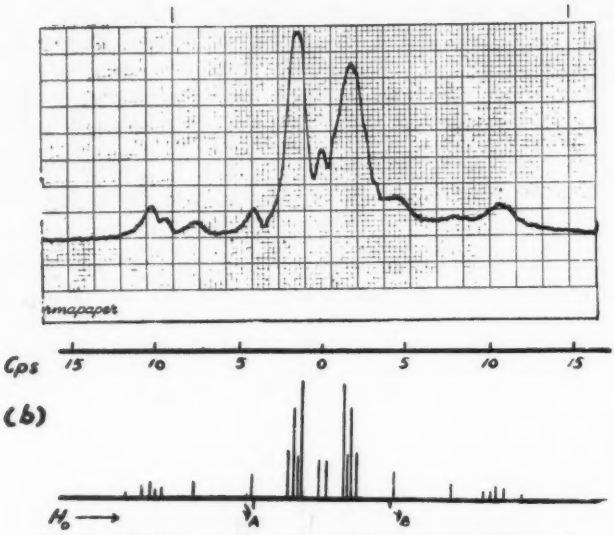

FIG. 3. H^1NMR spectrum of *para*-chlorotoluene at 40 mc./sec.
(*a*) Experimental, (*b*) Calculated: 1 cm. = 3·138 Cps.

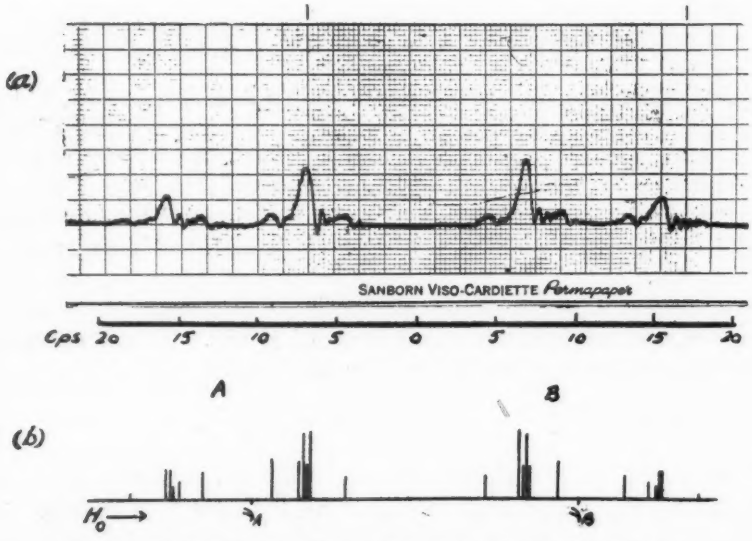

FIG. 4. H^1NMR spectrum of *para*-Chloroiodobenzene at 40 mc./sec.
(*a*) Experimental, (*b*) Calculated: 1 cm. = 3·184 Cps.

So, tentatively putting L = N (N being already) known K may be determined from every one of the four equations obtained above. Now, the roots of E, which yield values of K that are positive and close to each other and also lying in the range estimated from the known *meta* H–H coupling constants should be chosen as the proper roots E_3 and E_4. The corresponding equations involving K and L^2 can then be solved to obtain K and L.

Now the other roots E_1 and E_2 can be readily determined and if the lines 2 and 4, involving these energy levels, are satisfactorily accounted for in the observed spectrum, a check on the identification of lines 5 to 8 is obtained.

Sometimes, it may be possible, in practice, to find more than two pairs of lines satisfying the above condition, or one of the lines in a pair may not be observed if its intensity is very low,* so that an unambiguous assignment is not readily obtained. Some trial and error calculations will then be necessary to decide upon the proper assignment. Further, at two stages in the above procedure, firstly for the identification of lines 1 and 3, and secondly for determining the proper roots E_3 and E_4, a knowledge of approximate values of the coupling constants is said to be necessary. This, however, does not place any drastic limitation on the method (except that more trial and error calculations may be necessary) as any assignment is ultimately checked completely for internal consistency.

After satisfactorily assigning lines 1 to 8 if some lines in the observed spectrum are still left unassigned, they may be assigned properly to transitions 9 to 12 and the value of M may be calculated.†

The relative signs of the coupling constants cannot be determined in this analysis, and all the coupling constants were assumed to be positive for the spectra analyzed.

4. Results

Following the method described in the preceding section the lines in the spectrum of *p*-bromochlorobenzene [Fig. 2 (*a*)] are assigned in the following manner:

* Even if one of the pair of lines is identified the corresponding root of Eq. (2) may be determined.

† It may be noted that the value of M is very sensitive to slight errors in the line positions (even within the limits of experimental error) and therefore an approximate value of M may be estimated such that the calculated frequency agrees with the observed, within experimental error. It is not usually possible to determine the sign of M, as this can be done only if the intensities are accurately known, and thus it is difficult to find which of the two *meta* H–H coupling constants (J_A and J_B) is larger.

The lines at 1·50 and 10·40 cps., with respect to the centre of the spectrum, were first assigned to the transitions 3 and 1 respectively. From this we obtain $N = 8{\cdot}9$ cps. and $[(\nu_0\delta)^2 + N^2]^{\frac{1}{2}} = 11{\cdot}9$ cps. The two lines at 4·30 and 7·70 cps. were assigned to the transitions 6 and 7 and the line at 0 cps. was taken as one of the transitions 5 and 8.* Finally the line at 9·81 cps. was assigned to the transition 10.

The assignment of lines in the spectra of *p*-chlorotoluene and *p*-chloroiodobenzene was done in the same manner as above.

The parameters obtained in the analyses of these three spectra are given in Table II. The line frequencies and relative intensities calculated on the basis of these parameters, along with the observed line frequencies for *p*-bromochlorobenzene, *p*-chlorotoluene and *p*-chloroiodobenzene, are given in Table III, while the calculated spectra are shown in Figs. 2 (*b*), 3 (*b*) and 4 (*b*) respectively.

TABLE II

Values of the parameters obtained from the analyses (the values obtained by RS‡ are given for comparison)*

	Compound	$\nu_0\delta$	J_0^{III}	J_m^{III}		J_p^{III}
				1	2	
1.	*P*-bromochlorobenzene ..	7·9	$8{\cdot}6_5$	2·9	2·4	$0{\cdot}2_5$
	Values of RS ..	7·1	9·1	(Range 1·5–2·0)		0
2.	*P*-chlorotoluene ..	8·3	$8{\cdot}3_5$	2·7	2·2	$0{\cdot}3_5$
	Values of RS ..	5·3	9·1	(Range 1·5–2·0)		0
3.	*P*-chloroiodobenzene ..	20·7	8·4	2·7	2·2	0·3
	Values of R. S. ..	20·8	9·0	1·6		0

* All the values are given in cps. The error involved in any of the parameters is about ±0·2 cps.

‡ The $\nu_0\delta$ values in reference 3 are multiplied by (40/29·92) to compare with the values in the present work.

* The lines at 10·91 and 1·10 also appear to be a probable pair of lines to be assigned to either the transitions 6 and 7 or 5 and 8. But this was finally discarded as the assignment on this basis does not account for the line at 0 cps.

TABLE III

Calculated transition frequencies and relative intensities, and observed frequencies for* p-*bromochlorobenzene,* p-*chlorotoluene and* p-*chloroiodobenzene*

Transition No.†	*P*-bromochlorobenzene			*P*-chlorotoluene			*P*-chloroiodobenzene		
	$\nu_{cal.}$	$\nu_{obs.}$	$I_{cal.}$	$\nu_{cal.}$	$\nu_{obs.}$	$I_{cal.}$	$\nu_{cal.}$	$\nu_{obs.}$	$I_{cal.}$
5	11·90	..	0·05	11·82	..	0·07	18·02	18·07	0·13
2	11·06	10·91	0·21	10·78		0·24	15·65		0·60
1	10·40		0·25	10·36	10·36	0·28	15·60		0·61
		10·40						15·60	
9	10·16		0·13	9·97		0·14	15·42		0·30
10	9·79	9·81	0·15	9·61	9·41	0·17	14·96		0·34
6	7·65	7·70	0·29	7·71	7·73	0·32	13·45	13·50	0·56
7	4·25	4·30	0·42	4·31	4·33	0·46	9·05	9·10	0·82
11	1·74		0·87	1·93		0·86	7·31		0·70
3	1·50	1·50	1·75	1·66	1·66	1·72	6·89	6·89	1·39
12	1·37		0·85	1·57		0·83	6·84		0·66
4	1·11	1·10	2·23	1·27		2·22	6·68		1·45
8	0·00	0·00	0·61	0·20	0·20	0·72	4·48	4·53	0·47

(Calculated and observed frequencies are given in cps., for a half of the spectrum, with respect to the centre $\frac{1}{2}(\nu_A + \nu_B)$. $I_{cal.}$ stands for the calculated relative intensity.)

* Average standard deviations for the observed line frequency determinations for *p*-bromochlorobenzene, *p*-chlorotoluene and *p*-chloroiodobenzene are 0·12, 0·07 and 0·13 respectively.

† Nos. as in Table I.

The parameters are all obtained assuming $\nu_A > \nu_B$ but it is not possible to determine, from the analysis, which pair of nuclei are shielded more. In the case of *p*-chloroiodobenzene, however, by comparing with the results obtained by Corio and Dailey[6] on the chemical shifts in monosubstituted

benzenes, the two protons *ortho* to chlorine may be expected to be shielded more.

Note added in proof.—Schæffer and Schneider (*J. Chem. Phys.*, 1960, **32**, 1218) observe that a methyl group gives rise to spin-spin coupling with the ring protons and that this coupling is strongest with the protons *ortho* to the group, resulting usually in a broadening of the spectrum of these protons, and utilised this fact to identify the transitions of *ortho* and *meta* protons in several *para*-substituted toluenes. On this basis the protons *ortho* to methyl group in *p*-chlorotoluene may be taken to be shielded more as the half of this spectrum on the higher field is clearly broadened [*see* Fig. 3 (*a*)].

5. DISCUSSION

The agreement between the calculated and observed spectra, for all the three cases, as seen from Table III and Figs. 2, 3 and 4, is satisfactory, and the method of analysis therefore appears to be reliable.

The corresponding values of the parameters obtained by RS for all these cases are also given in Table II for comparison.

The *ortho*-coupling constants (J_0^{HH}) obtained by RS are all consistently larger than the corresponding values obtained here. This is because of the assumption made by RS that $J' = 0$, and the value of J_0^{HH} determined by them corresponds to N in the present analysis. All the *meta* H–H coupling constants (J_m^{HH}) obtained here are outside the range of 1·5 to 2·0 cps. suggested by RS for these molecules. All the coupling constants observed here agree with the values of the *ortho*, *meta* aand *para* H–H coupling constants in substituted benzenes determined by earlier workers.

The value of $\nu_0\delta$ for *p*-chloroiodobenzene obtained here agrees very well with the value of RS (Table II). However, there is considerable discrepancy between the $\nu_0\delta$ values determined here and those of RS (converted to 40 mc./sec., as given in Table II) in the case of the other two compounds. The value of $\nu_0\delta$ is small in both these cases and is still smaller at 29·92 mc./sec. used by RS for the work. The assignment of the lines to the transitions is usually rendered difficult when $\nu_0\delta$ is small and this is probably the reason for the low values of $\nu_0\delta$ obtained by RS in these cases. As the present experiments are done at 40 mc./sec. the values reported here are expected to be more reliable than those of RS.

6. DEPENDENCE OF THE SPECTRUM ON THE CHEMICAL SHIFT

In view of the several difficulties involved in arriving at a correct assignment, it was thought worthwhile to calculate the spectra for some typical

values of $\nu_0\delta$, as the rest of the parameters remain approximately the same for all the *p*-disubstituted benzenes. The manner in which a typical half of the spectrum varies with $\nu_0\delta$ is schematically represented in Fig. 5. In the

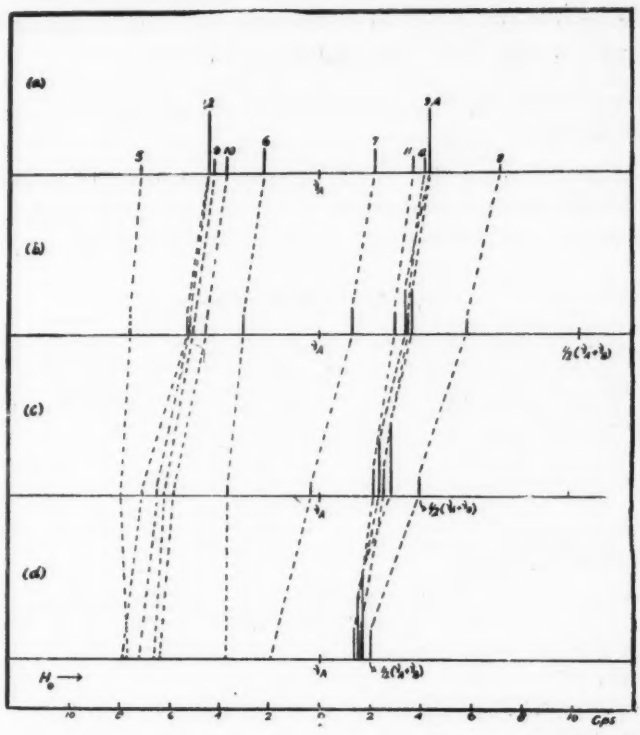

FIG. 5. Schematic representation of 'A' spectrum for different values of the chemical shift. (*a*) in the A_2X_2 limit, (*b*) $\nu_0\delta = 20{\cdot}7$ cps., (*c*) $\nu_0\delta = 7{\cdot}9$ cps., (*d*) $\nu_0\delta = 4$ cps.

Other parameters are N = 8·5 cps., L = 8·0 cps., K = 5·0cps. and M = 0·5 cps. The numbers correspond to the transitions given in Table I.

limit when $\nu_0\delta$ is large compared with the coupling constants (A_2X_2 case) the half of the spectrum is again symmetrical, in the positions of the lines as well as the intensities, about the centre ν_A. As $\nu_0\delta$ decreases the spectrum becomes gradually unsymmetrical with respect to the centre (ν_A), and the lines nearer to $\frac{1}{2}(\nu_A + \nu_B)$ increase in intensity while those away diminish in intensity, and some of them may even escape detection at small values of $\nu_0\delta$. The spectra (*b*) and (*c*) in Fig. 5 are the same as those of *p*-chloroiodobenzene and *p*-bromochlorobenzene respectively. The spectrum (*d*)

in Fig. 5 is calculated for $\nu_0\delta = 4{\cdot}0$ cps. Other parameters used in the calculation are:

$$\left.\begin{array}{ll} K = 5{\cdot}0 \text{ cps.} & N = 8{\cdot}5 \text{ cps.} \\ M = 0{\cdot}5 \text{ cps.} & L = 8{\cdot}0 \text{ cps.} \end{array}\right\}. \qquad (5)$$

These parameters in Eq. (5) are also used in the calculation of the spectrum (*a*) in the figure.

It can be seen from Fig. 5 that the spectrum depends on the chemical shift in a rather complicated manner, but the schematic variation shown in this diagram may be useful in analyzing spectra of this type.

7. ACKNOWLEDGEMENTS

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NUCLEAR MAGNETIC RESONANCE SPECTRA FOR A SYSTEM ABC OF SPIN ½ NUCLEI AND THEIR LINEWIDTHS

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1. Introduction

Recently, very extensive work (Pople *et al.*, 1959) has been done to investigate the NMR spectra of groups of interacting nuclei in different molecules in the liquid state. Here, as in any other spectrum calculations, energies and stationary state wave functions for the system in the absence of a time-dependent r.f. field have first to be calculated. The problem starts with finding the eigenfunctions and eigenvalues of the spin-dependent Hamiltonian of the system given by

$$\frac{\mathcal{H}}{\hbar} = E_0 = B + C$$

$$= -\sum_r \gamma_r H_{0r} m_r^0 + \tfrac{1}{2} \sum_{r \neq s} J_{rs} (\vec{I}_r \cdot \vec{I}_s)$$

$$= -\sum_r \omega_r m_r^0 + \tfrac{1}{2} \sum_{r \neq s} J_{rs} (m_r^0 m_s^0 + m_r^+ m_s^-) \qquad (1)$$

where the various groups of nuclei in the system are denoted by index r, the group r having the spin $\vec{I}_r$, γ_r is the gyromagnetic ratio of the nuclei and H_{0r} is a constant magnetic field effectively acting upon the group r in the z-direction. The notation

$$m_r^0 = I_{zr}$$

$$m_r^{\pm} = I_{xr} \pm i I_{yr},$$

where the operators I_{xr}, I_{yr} and I_{zr} represent the x, y and z components respectively of the spin vector $\vec{I}_r$ has been used here following Bloch (1956). This paper will hereafter be referred to as II. In the Hamiltonian, a coupling invariant against rotation and bilinear in the spin operators has been assumed with coupling constants $J_{rs} = J_{sr}$, independent of the external field.

This spin-spin interaction is the most effective part of the interaction for groups of nuclei within a molecule in the liquid state. The other term 'dipole-dipole interaction' is zero due to rotational motions in liquid.

The case of two groups of nuclei, where the total spin of one group is $\frac{1}{2}$, the exact solution of the problem reduces essentially to a diagonalisation of matrices of maximum order 2×2. The spectrum for this case has been worked out in detail by Banerjee *et al.* (1954). The two-group system is usually referred to as A_mB_n system, if the groups contain m and n nuclei respectively of the same species, and as A_mX_n, if the nuclei in each group are of different kinds with quite different gyromagnetic ratios. For a system AB of two interacting spin $\frac{1}{2}$ nuclei, the widths of the resonance lines have been calculated in II in terms of the longitudinal and transverse relaxation times T_{1r} and T_{2r} respectively exhibited separately by the nuclei $r = s, t$, where s and t are the two groups under the conditions considered by Wangsness and Bloch (1953) in the paper hereafter referred to as I.

For arbitrary number of nuclear groups, but only with equivalent nuclei in each group, perturbation calculations have been done and applied to specific systems by Anderson (1956), Alexander (1958) and various other authors. As reported in Anderson's paper, higher order corrections beyond the second order perturbation calculations gave better agreement with the experiment for some specific cases. Fessenden and Waugh (1959) and Alexander (1960) have analysed the ABC type spectra of some compounds, but they did not derive an explicit expression for the intensities and the frequencies of the various transitions and had to resort to numerical computations to diagonalise the two 3×3 matrices involved in the solution of the present problem. They have, however, evolved certain useful relationships such as the intensity and frequency sum rules which can be applied unambiguously only to cases involving moderately strong coupling. The use of these relationships made in conjunction with the inspection of the observed spectrum for this type of molecules helps to reduce the number of independent parameters (J_s and δ_s) to be evaluated and makes possible the assignment of proper values to them. Further no attempt has been made by these workers to calculate the linewidths for such spectra. Therefore, it is thought worthwhile to find the exact solutions for simple cases of 3 groups of interacting nuclei. We report here the exact solution of the problem of ABC system, without any restriction on the magnitude of the spin coupling relative to chemical shifts.

The method for calculating the linewidths with only the external dipole relaxation, as in Sec. 5 of II, has also been considered for this system in terms

of longitudinal and transverse relaxation times of individual nuclei from the general expression derived in II with strong spin coupling compared to the r.f. field $\vec{H}_1(t)$ and to the effects of relaxation.

2. Spectrum Calculation

In the system ABC, we have three nuclei s, t and u of spin ½, with Larmor frequencies ω_s, ω_t and ω_u respectively, so that

$$\begin{aligned} E_0 = &- (\omega_s m_s^0 + \omega_t m_t^0 + \omega_u m_u^0) + J_1 \{m_s^0 m_t^0 + \tfrac{1}{2}(m_s^+ m_t^- \\ &+ m_t^+ m_s^-)\} + J_2 \{m_s^0 m_u^0 + \tfrac{1}{2}(m_s^+ m_u^- + m_u^+ m_s^-)\} \\ &+ J_3 \{m_t^0 m_u^0 + \tfrac{1}{2}(m_t^+ m_u^- + m_u^+ m_t^-)\} \end{aligned} \tag{2}$$

with

$$J_{st} = J_{ts} = J_1$$

$$J_{su} = J_{us} = J_2$$

$$J_{tu} = J_{ut} = J_3.$$

We take our initial complete set of kets as the product of eigen kets of individual nuclei without the interaction $|m_s\rangle\ |m_t\rangle\ |m_u\rangle$, in the representation where m_r^0 and I_r^2 are diagonal with eigenvalues of $m_r^0 = m_r$, $(r = s, t, u)$. We label these kets in short as $|m_s m_t m_u\rangle$. The proper eigen kets for the Hamiltonian given by equation (2) will then be some linear combinations of $|m_s m_t m_u\rangle$ kets. Since here, $\sum_r m_r^0$ commutes with our total Hamiltonian $\mathcal{H}$, we can label the proper eigen kets of the system with a number M, the sum of the eigenvalues of m_s^0, m_t^0 and m_u^0.

It can be easily seen that the proper kets for $M = \pm 3/2$ can be only $|\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\rangle$ and $|-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\rangle$ respectively. For $M = \pm \frac{1}{2}$, the eigen states will be linear combinations of the states $|\pm\frac{1}{2}, \pm\frac{1}{2}, \mp\frac{1}{2}\rangle$, $|\pm\frac{1}{2}, \mp\frac{1}{2}, \pm\frac{1}{2}\rangle$ and $|\mp\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}\rangle$. Now, if we write the eigen state

$$|g(M)\rangle = \sum_{m_s m_t m_u} \langle m_s m_t m_u\,|g(M)\rangle\,|m_s m_t m_u\rangle, \tag{3}$$

the transformation functions for $M = -3/2$ and $M = +3/2$ can be written as

$$\langle m_s m_t m_u\,|E(-\tfrac{3}{2})\rangle = \delta_{m_s,-\frac{1}{2}}\,\delta_{m_t,-\frac{1}{2}}\,\delta_{m_u,-\frac{1}{2}} \tag{4}$$

and

$$\langle m_s m_t m_u\,|E(\tfrac{3}{2})\rangle = \delta_{m_s,\frac{1}{2}}\,\delta_{m_t,\frac{1}{2}}\,\delta_{m_u,\frac{1}{2}} \tag{5}$$

respectively, with the corresponding values of energy in units of $\hbar$ given by,

$$E(-\tfrac{3}{4}) = \tfrac{3}{2}\,\overline{\omega} + \tfrac{1}{4}(J_1 + J_2 + J_3) \tag{6}$$

and

$$E(\tfrac{3}{4}) = -\tfrac{3}{2}\,\omega + \tfrac{1}{4}(J_1 + J_2 + J_3). \tag{7}$$

Here ω is the average Larmor frequency

$$\frac{\omega_s + \omega_t + \omega_u}{3}$$

of the three nuclei.

For the states with $M = \pm\frac{1}{2}$, we can get the transformation functions by solving the corresponding sets of homogeneous equations

$$\sum_{m'_s m'_t m'_u} \langle m'_s m'_t m'_u \mid g(M)\rangle \{\langle m_s m_t m_u \mid E_0 \mid m'_s m'_t m'_u\rangle - E\delta_{m_s m'_s}\delta_{m_t m'_t}\delta_{m_u m'_u}\} = 0. \tag{8}$$

Thus the secular determinants, to be solved for $M = \pm\frac{1}{2}$ for getting the eigenvalues E and the transformation functions, are

$$\begin{vmatrix} Y^{\pm} - \dfrac{J_1+J_2+J_3}{4} \mp \dfrac{\overline{\omega}}{2} - E & \dfrac{J_3}{2} & \dfrac{J_2}{2} \\ \dfrac{J_3}{2} & Y_2^{\pm} - \dfrac{J_1+J_2+J_3}{4} \mp \dfrac{\overline{\omega}}{2} - E & \dfrac{J_1}{2} \\ \dfrac{J_2}{2} & \dfrac{J_1}{2} & Y_3^{\pm} - \dfrac{J_1+J_2+J_3}{2} \mp \dfrac{\overline{\omega}}{2} - E \end{vmatrix} = 0 \tag{9}$$

with

$$\begin{aligned} Y_1^{\pm} &= \frac{J_1}{2} \pm \frac{\delta_1 - 2\delta_2}{3} \\ Y_2^{\pm} &= \frac{J_2}{2} \pm \frac{\delta_2 - 2\delta_1}{3} \\ Y_3^{\pm} &= \frac{J_3}{2} \pm \frac{\delta_1 + \delta_2}{3} \end{aligned} \tag{10}$$

where the chemical shifts δ_1 and δ_2 are given by

$$\delta_1 = \omega_s - \omega_t$$

and

$$\delta_2 = \omega_s - \omega_u.$$

These determinants are expanded so that the solutions of resulting cubic equations in E for $M = \pm \frac{1}{2}$ give the eigenvalues

$$E_i\left(\pm\frac{1}{2}\right) = \mp\frac{\varpi}{2} - \frac{1}{12}(J_1 + J_2 + J_3) - \frac{b^{\pm}}{a^{\pm}} f_i(\theta^{\pm}), \tag{11}$$

for $i = 1, 2, 3$. In equation (11),

$$\theta^{\pm} = \frac{(b^{\pm})^2}{(a^{\pm})^3}, \tag{12}$$

$$\left.\begin{aligned} f_1(\theta) &= \frac{\left[1 + \sqrt{\frac{4}{27\theta} + 1}\right]^{\frac{1}{3}} + \left[1 - \sqrt{\frac{4}{27\theta} + 1}\right]^{\frac{1}{3}}}{(2\theta)^{\frac{1}{3}}} \\ f_2(\theta) &= -\frac{f_1(\theta)}{2} + \sqrt{\frac{f_1^2(\theta)}{4} - \frac{1}{\theta f_1(\theta)}} \\ f_3(\theta) &= -\frac{f_1(\theta)}{2} - \sqrt{\frac{f_1^2(\theta)}{4} - \frac{1}{\theta f_1(\theta)}} \end{aligned}\right\} \tag{13}$$

with

$$\begin{aligned} a = &-\tfrac{1}{3}(Y_1^2 + Y_2^2 + Y_3^2 - Y_1Y_2 - Y_1Y_3 - Y_2Y_3) \\ &-\tfrac{1}{4}(J_1^2 + J_2^2 + J_3^2) \end{aligned} \tag{14}$$

and

$$\begin{aligned} b = &-\frac{2}{27}(Y_1 + Y_2 + Y_3)^3 + \tfrac{1}{4}(J_1^2Y_1 + J_2^2Y_2 + J_3^2Y_3) \\ &+\tfrac{1}{3}(Y_1 + Y_2 + Y_3)\{Y_1Y_2 + Y_1Y_3 + Y_2Y_3 \\ &-\tfrac{1}{4}(J_1^2 + J_2^2 + J_3^2)\} - Y_1Y_2Y_3 - \tfrac{1}{4}J_1J_2J_3. \end{aligned} \tag{15}$$

The functions $f_1(\theta)$, $f_2(\theta)$ and $f_3(\theta)$ are tabulated for a wide range of θ by Salzer (1958). From the expression for 'a', one can easily see that for real values of J_1, J_2, J_3, δ_1 and δ_2, we will always get the value of 'a' negative and hence the value of θ will always be negative. Further, in our case, since all the roots will be real, θ will have the values such that

$$-\frac{4}{27} < \theta < 0.$$

The orthonormalised eigenvectors corresponding to the characteristic values $E_i(\pm\frac{1}{2})$ of the matrices

$$\begin{bmatrix} Y_1^{\pm} - \frac{J_1+J_2+J_3}{4} \mp \frac{\omega}{2} & \frac{J_3}{2} & \frac{J_2}{2} \\ \frac{J_3}{2} & Y_2^{\pm} - \frac{J_1+J_2+J_3}{4} \mp \frac{\omega}{2} & \frac{J_1}{2} \\ \frac{J_2}{2} & \frac{J_1}{2} & Y_3^{\pm} - \frac{J_1+J_2+J_3}{4} \mp \frac{\omega}{2} \end{bmatrix}$$

can be denoted by

$$\begin{bmatrix} C_{i1}^{\pm} \\ C_{i2}^{\pm} \\ C_{i3}^{\pm} \end{bmatrix}.$$

The explicit values of these in our case are obtained as

$$\begin{bmatrix} C_{i1}^{\pm} \\ C_{i2}^{\pm} \\ C_{i3}^{\pm} \end{bmatrix} = \begin{bmatrix} \eta_{i1}^{\pm} \{(\eta_{i1}^{\pm})^2 + (\eta_{i2}^{\pm})^2 + (\eta_{i3}^{\pm})^2\}^{-\frac{1}{2}} \\ \eta_{i2}^{\pm} \{(\eta_{i1}^{\pm})^2 + (\eta_{i2}^{\pm})^2 + (\eta_{i3}^{\pm})^2\}^{-\frac{1}{2}} \\ \eta_{i3}^{\pm} \{(\eta_{i1}^{\pm})^2 + (\eta_{i2}^{\pm})^2 + (\eta_{i3}^{\pm})^2\}^{-\frac{1}{2}} \end{bmatrix} \tag{16}$$

where

$$\eta_{i1}^{\pm} = \frac{J_2}{2}\left\{Y_2^{\pm} - \frac{1}{6}(J_1 + J_2 + J_3) + \frac{b^{\pm}}{a^{\pm}} f_i(\theta^{\pm})\right\} - \frac{J_1 J_3}{4}$$

$$\eta_{i2}^{\pm} = \frac{J_1}{2}\left\{Y_1^{\pm} - \frac{1}{6}(J_1 + J_2 + J_3) + \frac{b^{\pm}}{a^{\pm}} f_i(\theta^{\pm})\right\} - \frac{J_2 J_3}{4}$$

$$\eta_{i3}^{\pm} = \frac{J_3^2}{4} - \left\{Y_1^{\pm} - \frac{1}{6}(J_1 + J_2 + J_3) + \frac{b^{\pm}}{a^{\pm}} f_i(\theta^{\pm})\right\} \times \left\{Y_2^{\pm} - \frac{1}{6}(J_1 + J_2 + J_3) + \frac{b^{\pm}}{a^{\pm}} f_i(\theta^{\pm})\right\}. \tag{17}$$

Now the transformation functions for the states with $E(\pm \frac{1}{2})$ can be easily written. They are

$$\langle m_s m_t m_u \mid E_i(+\tfrac{1}{2})\rangle = C_{i1}^{+}\delta_{m_s\frac{1}{2}}\delta_{m_t\frac{1}{2}}\delta_{m_u-\frac{1}{2}} + C_{i2}^{+}\delta_{m_s\frac{1}{2}}\delta_{m_t-\frac{1}{2}}\delta_{m_u\frac{1}{2}} + C^{+}{}_{i3}\delta_{m_s-\frac{1}{2}}\delta_{m_t\frac{1}{2}}\delta_{m_u\frac{1}{2}} \tag{18}$$

and

$$\langle m_s m_t m_u \mid E_i(-\tfrac{1}{2})\rangle = C_{i1}^{-}\delta_{m_s-\frac{1}{2}}\delta_{m_t-\frac{1}{2}}\delta_{m_u\frac{1}{2}} + C_{i2}^{-}\delta_{m_s-\frac{1}{2}}\delta_{m_t\frac{1}{2}}\delta_{m_u-\frac{1}{2}} + C_{i3}^{-}\delta_{m_s\frac{1}{2}}\delta_{m_t-\frac{1}{2}}\delta_{m_u-\frac{1}{2}}. \tag{19}$$

The magnetic dipole transitions due to a weak r.f. field are possible only between the states

$$|\,E(-\tfrac{3}{2})\rangle,\quad |\,E_i(-\tfrac{1}{2})\rangle;\quad |\,E_i(-\tfrac{1}{2})\rangle,\quad |\,E_j(+\tfrac{1}{2})\rangle$$

and

$$|\,E_j(+\tfrac{1}{2})\rangle,\quad |\,E(+\tfrac{3}{2})\rangle$$

where $i, j = 1, 2, 3$. The relative intensities of these 15 lines, for the transitions between different allowed pairs of states $|\,g\rangle$, $|\,g'\rangle$, can be calculated by evaluating the quantities

$$|\,g\,|\sum_r I_{xr}\,|\,g'\,\rangle\,|^2 \tag{20}$$

In Table I, we give the relative intensities for allowed transitions.

TABLE I

Transitions	No. of lines	Frequency ν, in cycles/sec.	Relative intensities
$E(-\frac{3}{2}) \rightarrow E_i(-\frac{1}{2})$ $i = 1, 2, 3$	3	$\frac{1}{2\pi}\left[\overline{\omega} + \frac{1}{3}(J_1 + J_2 + J_3) + \frac{b^-}{a^-} f_i(\theta^-)\right]$	$(C_{i1} + C_{i2} + C_{i3})^2$
$E_i(-\frac{1}{2}) \rightarrow E_j(\frac{1}{2})$ $i, j = 1, 2, 3$	9	$\frac{1}{2\pi}\left[\overline{\omega} - \frac{b^-}{a^-} f_i(\theta^-) + \frac{b^+}{a^+} f_j(\theta^+)\right]$	$(C^+_{j2}C^-_{i1} + C^+_{j1}C^-_{i2} + C^+_{j3}C^-_{i1} + C^+_{j1}C^-_{i3} + C^+_{j3}C^-_{i2} + C^+_{j2}C^-_{i3})^2$
$E_j(\frac{1}{2}) \rightarrow E(\frac{3}{2})$ $j = 1, 2, 3$	3	$\frac{1}{2\pi}\left[\overline{\omega} - \frac{1}{3}(J_1 + J_2 + J_3) - \frac{b^+}{a^+} f_j(\theta^+)\right]$	$(C_{j1} + C_{j2} + C_{j3})^2$

3. LINEWIDTHS

Bloch has explicitly given the general expression for the linewidths in Sec. 5 of II, where he has assumed a spin-spin coupling term C strong in comparison to the r.f. field $\vec{H}_1(t)$ and to the effects of relaxation (considering only the external dipole relaxation). Following the same notations and assuming the isotropy of molecular surroundings, which is a good

approximation for molecules in liquid state, Bloch's expression for the linewidth for the transition between the stationary states b and a, is given by

$$\Gamma_{ab} = \sum_{r} \Gamma^{p}{}_{aa} + \Gamma^{p}{}_{bb} - 2\Gamma^{0}{}_{ab} \tag{21}$$

with

$$\begin{aligned}\Gamma^{p}{}_{gg'} = \sum_{r} \phi_r{}^{p} \{ &\langle g \mid \mathrm{I}_r{}^{0} \mid g+p \rangle \langle g'+p \mid \mathrm{I}_r{}^{0} \mid g' \rangle \\ &+ \tfrac{1}{2} \langle g \mid \mathrm{I}_r{}^{-1} \mid g+p \rangle \langle g'+p \mid \mathrm{I}_r{}^{+1} \mid g' \rangle \\ &+ \tfrac{1}{2} \langle g \mid \mathrm{I}_r{}^{+1} \mid g+p \rangle \langle g'+p \mid \mathrm{I}_r{}^{-1} \mid g' \rangle \}\end{aligned} \tag{22}$$

where

$$\mathrm{I}_r{}^{0} = m_r{}^{0},$$

$$\mathrm{I}_r{}^{\pm 1} = m_r{}^{\pm},$$

$\mid g \rangle$ is one of the stationary eigen kets for the system and the coefficients $\phi_r{}^{p}$, characteristics of molecular surroundings, are given by equation (5.25) with (5.26) and (5.27) of II.

For calculating the linewidths of transition spectrum in our case, we neglect the slight variations of the coefficients $\phi_r{}^{p}$ due to chemical shifts and spin couplings, so that

$$\phi_r{}^{\mathrm{E}(3/2)-\mathrm{E}_i(-\frac{1}{2})} = \phi_r{}^{\mathrm{E}_i(-\frac{1}{2})-\mathrm{E}_j(+\frac{1}{2})} = \phi_r{}^{\mathrm{E}_i(\frac{1}{2})-\mathrm{E}(3/2)} = \phi_r{}^{\bar{\omega}}$$

and

$$\phi_r{}^{\mathrm{E}_i(\frac{1}{2})-\mathrm{E}_j(\frac{1}{2})} = \phi_r{}^{\mathrm{E}_i(-\frac{1}{2})-\mathrm{E}_j(-\frac{1}{2})} = \phi_r{}^{0}$$

for

$$i,\ j = 1,\ 2,\ 3.$$

Now, replacing $2\phi'_{11}$ and $\phi^{0}{}_{11}$ of equations (5.3) and (5.4) of I, by $\phi_r{}^{-\bar{\omega}}$ and $\phi_r{}^{0}$, we get

$$\phi_r{}^{-\bar{\omega}} = \frac{1}{(1+e^{-k})\,\mathrm{T}_{1r}} \tag{23}$$

$$\phi_r{}^{0} = \frac{1}{\mathrm{T}_{2r}} - \frac{1}{2\mathrm{T}_{1r}} \tag{24}$$

where

$$\mathrm{K} = \frac{\hbar\bar{\omega}}{k\mathrm{T}},$$

k being the Boltzmann constant and T the absolute temperature of the system. Since

$$\phi_r{}^{\bar{\omega}} = e^{-k}\phi_r{}^{-\bar{\omega}},$$

all the coefficients $\phi_r{}^p$ for evaluating $\Gamma^p{}_{gg'}$ can be known approximately in terms of the longitudinal and transverse relaxation times T_{1r} and T_{2r} which are exhibited separately by the nuclei under the conditions considered in I.

We can easily verify that for our system, we have only the following non-zero matrix elements for $I_r{}^0$ and $I_r{}^\pm$:—

$$\langle E_i(-\tfrac{1}{2}) \mid I_s' \mid E(-\tfrac{3}{2})\rangle = \langle E(-\tfrac{3}{2}) \mid I_s{}^{-1} \mid E_i(-\tfrac{1}{2})\rangle = C_{is}{}^-$$

$$\langle E_i(-\tfrac{1}{2}) \mid I_t' \mid E(-\tfrac{3}{2})\rangle = \langle E(-\tfrac{3}{2}) \mid I_t{}^{-1} \mid E_i(-\tfrac{1}{2})\rangle = C_{it}{}^-$$

$$\langle E_i(-\tfrac{1}{2}) \mid I_u' \mid E(-\tfrac{3}{2})\rangle = \langle E(-\tfrac{3}{2}) \mid I_u{}^{-1} \mid E_i(-\tfrac{1}{2})\rangle = C_{iu}{}^-$$

$$\langle E_i(-\tfrac{1}{2}) \mid I_s{}^{-1} \mid E_j(\tfrac{1}{2})\rangle = \langle E_j(\tfrac{1}{2}) \mid I_s{}^1 \mid E_i(-\tfrac{1}{2})\rangle = C_{js}{}^+C_{iu}{}^- + C_{ju}{}^+C_{it}{}^-$$

$$\langle E_i(-\tfrac{1}{2}) \mid I_t{}^{-1} \mid E_j(\tfrac{1}{2})\rangle = \langle E_j(\tfrac{1}{2}) \mid I_t{}^1 \mid E_i(-\tfrac{1}{2})\rangle = C_{jt}{}^+C_{iu}{}^- + C_{ju}{}^+C_{is}{}^-$$

$$\langle E_i(-\tfrac{1}{2}) \mid I_u{}^{-1} \mid E_j(\tfrac{1}{2})\rangle = \langle E_j(\tfrac{1}{2}) \mid I_u{}^1 \mid E_i(-\tfrac{1}{2})\rangle = C_{jt}{}^+C_{is} + C_{js}{}^+C_{it}{}^-$$

$$\langle E_j(\tfrac{1}{2}) \mid I_s{}^{-1} \mid E(\tfrac{3}{2})\rangle = \langle E(\tfrac{3}{2}) \mid I_s{}^1 \mid E_j(\tfrac{1}{2})\rangle = C_{js}{}^+$$

$$\langle E_j(\tfrac{1}{2}) \mid I_t{}^{-1} \mid E(\tfrac{3}{2})\rangle = \langle E(\tfrac{3}{2}) \mid I_t{}^1 \mid E_j(\tfrac{1}{2})\rangle = C_{jt}{}^+$$

$$\langle E_j(\tfrac{1}{2}) \mid I_u{}^{-1} \mid E(\tfrac{3}{2})\rangle = \langle E(\tfrac{3}{2}) \mid I_u{}^1 \mid E_j(\tfrac{1}{2})\rangle = C_{ju}{}^+$$

$$\langle E(\tfrac{3}{2}) \mid I_r{}^0 \mid E(\tfrac{3}{2})\rangle = -\tfrac{1}{2},\ \langle E(-\tfrac{3}{2}) \mid I_r{}^0 \mid E(-\tfrac{3}{2})\rangle = \tfrac{1}{2}$$

for $r = s, t, u$

$$\langle E_i(\pm\tfrac{1}{2}) \mid I_s{}^0 \mid E_j(\pm\tfrac{1}{2})\rangle = \pm\tfrac{1}{2}[C_{is}{}^\pm C_{js}{}^\pm + C_{it}{}^\pm C_{jt}{}^\pm \mp C_{iu}{}^\pm C_{ju}{}^\pm]$$

$$\langle E_i(\pm\tfrac{1}{2}) \mid I_t{}^0 \mid E_j(\pm\tfrac{1}{2})\rangle = \pm\tfrac{1}{2}[C_{is}{}^\pm C_{js}{}^\pm \mp C_{it}{}^\pm C_{jt}{}^\pm + C_{iu}{}^\pm C_{ju}{}^\pm]$$

$$\langle E_i(\pm\tfrac{1}{2}) \mid I_u{}^0 \mid E_j(\pm\tfrac{1}{2})\rangle = \pm\tfrac{1}{2}[\mp C_{is}{}^\pm C_{js}{}^\pm + C_{it}{}^\pm C_{jt}{}^\pm + C_{iu}{}^\pm C_{ju}{}^\pm].$$

With these expressions, $\Gamma^p{}_{gg}$, and $\Gamma^0{}_{gg'}$ can be calculated for all g and g' from the equation (22). Finally equation (21) directly gives the linewidths for

the resonance lines. Since the analytical expressions for these are very complicated, they are not reported here, but it is clear that for any set of values for J_1, J_2, J_3, δ_1 and δ_2 we can always calculate the linewidths by the procedure outlined above.

4. DISCUSSION

To analyse the experimental results of the system ABC, one has to proceed by a method of trial and error and assign some of the observed transitions to definite initial and final states by a clever guess, and then deduce from the values of their measured frequencies and intensities, the relevant constants J_1, J_2, J_3, $\overline{\omega}$, δ_1 and δ_2, using Table I. The relationships evolved by Fessenden and Waugh when used in conjunction with these calculations will reduce the number of independent parameters. From this set of values, one can find out the relative intensities and frequencies of all other transitions theoretically and try to see that all the transitions are described together in a self-consistent manner. Thus even if all the 15 lines are not well resolved in the experimental data it is possible to give unique solution for J_1, J_2, J_3, $\overline{\omega}$, δ_1 and δ_2.

There has so far been no attempt to verify the theoretical expressions for the linewidths even for the system AB of spin $\frac{1}{2}$ nuclei. This is probably due to the fact that the linewidths in question may be very small. It is hoped that as the precision in the experimental techniques of high resolution nuclear magnetic resonance spectroscopy increases, it may be possible to compare the results of linewidths for not only the system AB, but also for the more complicated system ABC and to get more information about the mechanism of relaxation.

The n.m.r. spectra of some trisubstituted benzenes have been analysed in our laboratory on the basis of these equations and the results will soon be communicated for publication.

SUMMARY

The exact solution for the splitting up of nuclear resonance lines due to J couplings of spins between three like nuclei of spin $\frac{1}{2}$ with relative chemical shifts is worked out. Here no specific assumption about the magnitude of the coupling constants compared to the chemical shifts is made. It is shown how the linewidths of all the resonance lines can be calculated for the present case from the general expressions derived in Bloch's dynamical theory of nuclear induction with external dipole relaxation mechanism.

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CHANGES IN THE ELECTRON DENSITY DISTRIBUTION IN THE IONOSPHERE OVER AHMEDABAD ASSOCIATED WITH SOLAR FLARES AND MAGNETIC STORMS

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Introduction

The present paper contains data of electron density distribution in the ionosphere over Ahmedabad in a highly disturbed period in July 1959 and a brief discussion of the findings. From the vertical soundings made at the Physical Research Laboratory, the true heights of reflection of the various frequencies were calculated using the tables of Schmerling and Ventrice (1959) and modifying them for the magnetic latitude of Ahmedabad (Dip 34°). As is well known, what we get from the soundings are the virtual heights of reflection h' of pulses of different frequencies where

$$h' = \int_0^{h_0} \mu'(f, f_0)\, dh. \qquad (1)$$

In equation (1), μ' refers to the group refractive index for ordinary waves of frequency f, h is the height above ground, h_0 is the height of reflection of waves of frequency f_0; and f_0 is related to the electron density N by the relation

$$N = 1{\cdot}24 \times 10^4 f_0^2$$

where N is expressed as the number of electrons per cm.^{3}, and f_0 as Mc./sec.

μ' is a complicated function of f and N and the strength and direction of the earth's magnetic field. Knowing h' for different frequencies, we have to determine the values of the geometric height h. The equation can be solved only by numerical analysis, using a lamination method in which the integral is replaced by a discrete sum over a number of suitable strips (*see* Thomas and Vickers, 1958).

Equation (1) can be written as

$$h'(f) = \int_0^{f_0} \mu'(f, f_0) \frac{dh}{df_0} df_0. \tag{2}$$

The integral equation (2) can be treated as the limit of a matrix equation $= \mathrm{MD}h$.

The coefficients in the matrix equation can be solved either by inverting the matrix, or by a step-by-step solution for each strip. The accuracy can be increased as much as we desire by choosing sufficiently small intervals. For rapid reduction this method requires a digital computer which was not available.

The manual method of Schmerling (1958) allows for the effect of the earth's magnetic field, assumes only that the electron density increases monotonically with height and is convenient to use and sufficiently accurate. The true height corresponding to the frequency f_0 is given by

$$h(f_0) = \frac{1}{n} \sum_{1}^{i=n} h'(f_i) \tag{3}$$

where h' is measured in kilometers and the f_i's are the frequencies at which the virtual heights are read to give $h(f_0)$. The frequencies f_i depend on the end frequency f_0.

Using this method and the tables of coefficients given by Schmerling and Ventrice (1959) the values of the coefficients for the dip latitude of Ahmedabad which is 34° N. and the gyrofrequency 1·18 Mc./s. were interpolated. For calculating the coefficients, the values of dip angle and the total magnetic field at ionospheric heights are required to be known accurately. Schmerling's table provides the coefficients only up to 13·5 Mc./s. but since at Ahmedabad, the F_2 layer critical frequencies often go beyond 16 Mc./s. it became necessary to extend the column of coefficients to 16·5 Mc./s. by extrapolation. These coefficients which are in the form of ratios f_i/f_0 for given values of f_0, within the ranges given, define the sampling frequencies f_i at which h' are to be read from the h'–f curve to give $h(f_0)$. The sampling frequencies can be chosen either at 10 points or 5 points. We compared the results by both the 10-point and the 5-point methods and since they were found to agree well, we decided to adopt the 5-point analysis generally and use the 10-point method at frequencies near which there were rapid changes of h'. Table I gives the coefficients used.

TABLE I

10 *coefficients for calculating* h *from* h'f *over Ahmedabad*

	f_0 Mc./s.								
	16·5	13·5	12·0	10·5	9·0	7·5	6·0	4·5	3·0
f_i/f_0 ..	0·995	·995	·995	·995	·995	·995	·995	·994	·993
..	·965	·965	·965	·965	·965	·964	·963	·963	·962
..	·914	·912	·911	·910	·909	·908	·906	·905	·906
..	·841	·839	·838	·836	·835	·833	·830	·827	·824
..	·750	·748	·747	·745	·743	·741	·737	·733	·727
..	·641	·639	·638	·637	·635	·632	·629	·624	·616
..	·517	·515	·514	·513	·511	·509	·506	·501	·496
..	·380	·378	·377	·376	·375	·373	·370	·367	·366
..	·230	·230	·230	·229	·228	·227	·226	·225	·226
..	·077	·077	·077	·077	·077	·076	·076	·077	·078

TABLE II

5 *coefficients for calculating* h *from* h'f *over Ahmedabad*

	f_0 Mc./s.								
	16·5	13·5	12·0	10·5	9·0	7·5	6·0	4·5	3·0
f_i/f_0 ..	0·985	·984	·984	·984	·983	·983	·983	·982	·981
..	·880	·878	·877	·875	·874	·872	·870	·868	·867
..	·700	·696	·694	·693	·691	·688	·685	·680	·673
..	·450	·448	·447	·446	·444	·442	·440	·435	·432
..	·154	·154	·154	·153	·153	·152	·152	·152	·153

Tables of sampling frequencies f_1, $f_2 \ldots f_{10}$ for the 10-point method and of f_1, $f_2 \ldots f_5$ for the 5-point method were prepared by multiplying the

frequencies from 1 Mc./s. to 20 Mc./s. at 0·5 Mc./s. intervals by the above coefficients in the appropriate frequency ranges. To obtain the true height at a particular frequency f_0, the virtual heights at 10 (or 5) frequencies indicated opposite the value of f_0 in the table (not given here) are added up and their average found.

Later on, a procedure was adopted for the rapid reduction of h'-f curves to N(h) profiles. Each h'-f trace was sketched on a simple log graph paper with frequencies on a logarithmic scale. Three different transparent sliders were prepared with sampling ratios marked on them in the same scale for datum f_0 frequencies of 4·5, 10·5 and 16·5 Mc./s. Within the range of accuracy of the slider, it was then only necessary to align the datum with the frequency on the record for which h is required, to read off h' at marked points on the slider and to take the mean. This procedure is quicker and has the advantage that it serves to obtain the true height at any desired frequency on the h'-f curve.

The data presented here relate to the period when solar activity was exceptionally high. There were as many as seven solar flares of major importance between the 10th and 17th July 1959 and three great magnetic storms were associated with them. Table III lists the solar flares with their occurrence times in 75° E.M.T. and in Table IV are listed the three magnetic storms.

TABLE III

Short wave fade-outs

Date	Time of commencement	Importance	Ionospheric effects
10–7–1959	0710	3+	Slow
	1014	3+	G
13–7–1959 ..	0252	3	G
14–7–1959 ..	0825	3+	S
	1900	3+	Slow
16–7–1959 ..	1808	3	S
17–7–1959 ..	0214	3+	S

G—gradual; S—sudden

—(From the *Transactions of American Geophysical Union*, 1960, **41**, 87.)

TABLE IV

Date	Start of SC at Kodaikanal 75° E.M.T.	Date	Approx. end of storm 75° E.M.T.	Intensity	H in γ
11–7–1959	2128	12–7–1959	19xx	*m*	168
15–7–1959	1302	17–7–1959	04xx	*s*	785
17–7–1959	2138	19–7–1959	16xx	*ms*	327

—(From the *Indian Journal of Met. and Geophy.*, 1960, **11**, 86.)

Due to the kindness of the Director of the Alibag Observatory (Dr. P. R. Pisharoty), we are enabled to reproduce the H magnetograms of Alibag on these days (Fig. 1).

It can be seen that the storm on the 15th was of very severe type.

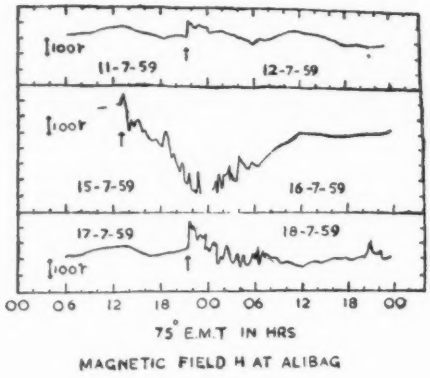
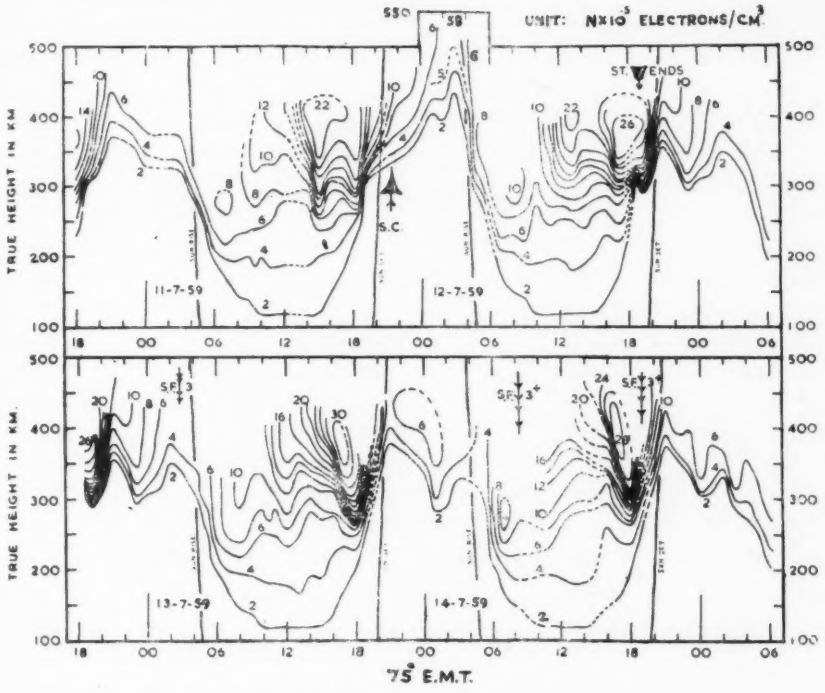


FIG. 1.

Results of true height analysis.—In Figs. 2 and 3 are plotted the electron densities at every 10 km. interval starting from the bottom of the E-layer during day, and of the F-layer during night. Lines of equal density were drawn at intervals of 2×10^5 el./c.c. Such a representation shows up the true changes of the heights of particular density levels. These results are based on the reduction of all hourly h'-f records. Some half-hourly records too were utilised, particularly when they showed somewhat different characteristics in comparison with the neighbouring hourly records. When an hourly record was missing, the one nearest to that one was taken for

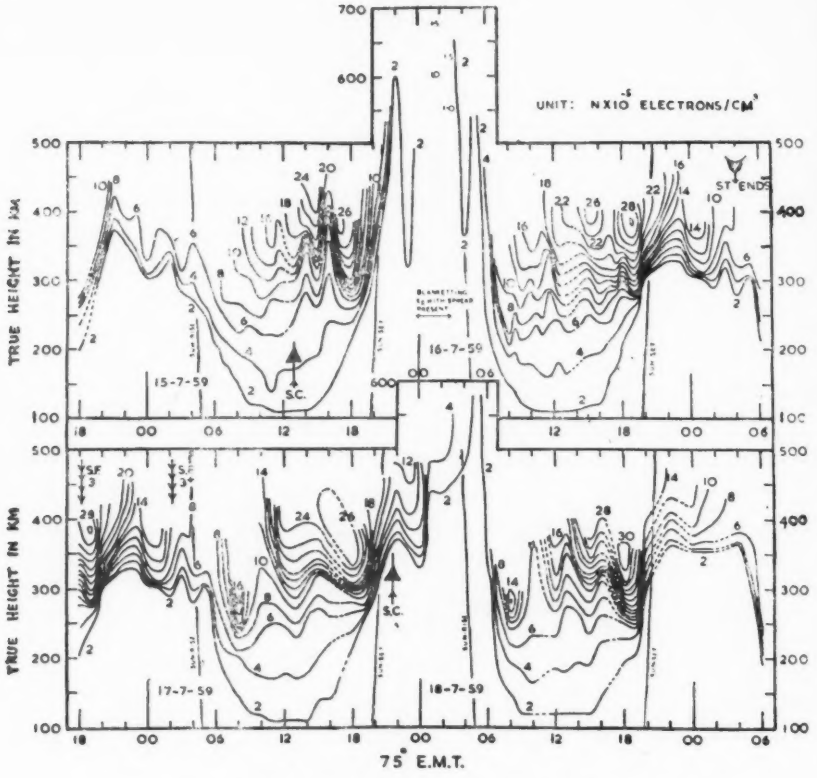


ELECTRON DENSITIES OVER AHMEDABAD 11 TO 14 JULY 1959

FIG. 2.

reduction. Whenever E-region cusps were not visible on the ionograms (due to absorption or other causes), the E–F transition was sketched in from the monthly median values of f_0E. As the F-layer is most sensitive to magnetic disturbances, it is believed that the present study will be able to throw some light on their characteristic features. We shall now discuss the results.

I. The storm on the 11th was preceded by a flare on the 10th. It was of the SC type and moderate in character. The time of onset of the storm at Alibag is marked on the diagram by a big arrowhead. The storm occurred at night and the oscillations built up in the F-region can be clearly seen. The peak oscillation took place at about 03 hrs. on the 12th, nearly 5½ hrs. after the onset of the storm. If we compare particular density levels on this night with those on the previous and the following night, we can see that the levels had gone up by more than 100 km. at 03 hrs. on the 12th.



ELECTRON DENSITIES OVER AHMEDABAD 15 TO 18 JULY 1959

FIG. 3.

The rise in height was associated with a fall in electron density. The storm ended at about 19 hrs. on the 12th.

The variation is better appreciated when we compare the density distribution on the 13th which was a magnetically quiet day. The distribution on the 14th was more or less similar to that on the 13th.

Another big solar flare was observed at 0825 hrs. on the 14th. This flare produced a sudden short-wave fade-out for over an hour and during that period, ionosondé records could not be obtained. It would be of interest to know whether the flare caused any immediate enhancement of ionization in the F-layer. However, radio pulses of relatively small power are inadequate to probe this.

Yet another solar flare occurred at 19 hrs. (about sunset) on the 14th but this could not be observed at Ahmedabad; it would have certainly caused changes in the ionosphere in the sunlit portions of the atmosphere.

II. The intense magnetic storm which commenced at 1302 hrs. on the 15th induced perturbations within an hour of its onset. The undulations were built up with increasing amplitude, the peak occurring sometime between 00 and 02 hrs. on the 16th. The exact peak intensity of the oscillations could not be followed owing to two reasons: (1) an unusually strong blanketing type of E_s occurred with multiple reflections and spread echoes in the ionograms, and since the maximum electron densities were low, the E_s partly blanketed the trace. (2) As the layer heights were very great, the trace might have gone beyond the scale of the record which was nearly 900 km. In any case it is evident that the amplitude of the oscillations were of the order of 300 km. The whole layer was dilated and this was accompanied by a steep fall in electron densities. The period of oscillations was roughly 2 hrs. in the beginning. It is curious to note that between 21 and 23 hrs., the $f_{\min.}$ trace suffered group retardation because of the presence of low-level ionization below the F-layer. The distribution of electrons below the F-layer could not however be determined with exactness.

The storm continued to influence the ionosphere till 19 hrs. on the 16th. Once its influence weakened, the electron densities increased and the layer heights dropped to 300–350 km.

III. Before discussing the last storm, we should like to make a remark on the high electron concentrations observed at relatively low levels between 250 and 280 km. at about 08 hrs. on the 17th and at about the same time on the 18th. We have calculated the total electron content n_T up to $h_m F_2$ at each hour on all these days. (These are given in the Appendix in units of 10^{11} el./cm.^{2} col.) The total electron content also shows peaks in the early morning hours on the 17th and 19th. The peak electron density of 26×10^5 el./cm.^{3} at 12 hour on the 17th was exceptionally high for July at that hour.

The storm which commenced at 2138 hrs. on the 17th showed similar perturbations but of less amplitude. The peak oscillation occurred at about 05 hrs. on the 18th, and the undulations continued till 16 hrs. on the 19th. The period of the oscillations was about 3 hrs. to start with.

The following points stand out:

(1) The perturbations produced by magnetic storms in low latitudes are mainly in the F-layer. The ionosphere below 200 km. remains relatively unaffected.

(2) During a magnetic storm the layer heights go up, accompanied by sharp falls in electron densities. There is comparatively little or no F-scatter.

(3) The total electron content also undergoes wide fluctuations during a storm. The daytime peak of n_T splits into several maxima as compared to a single peak on an undisturbed day. There is a tendency for the total content to be subdued during daytime when a magnetic storm is in progress.

(4) It is interesting to note that the daytime h_mF is definitely lower than h_pF$_2$ both on quiet and disturbed days (Figs. 4 *a* and 4 *b*). The difference

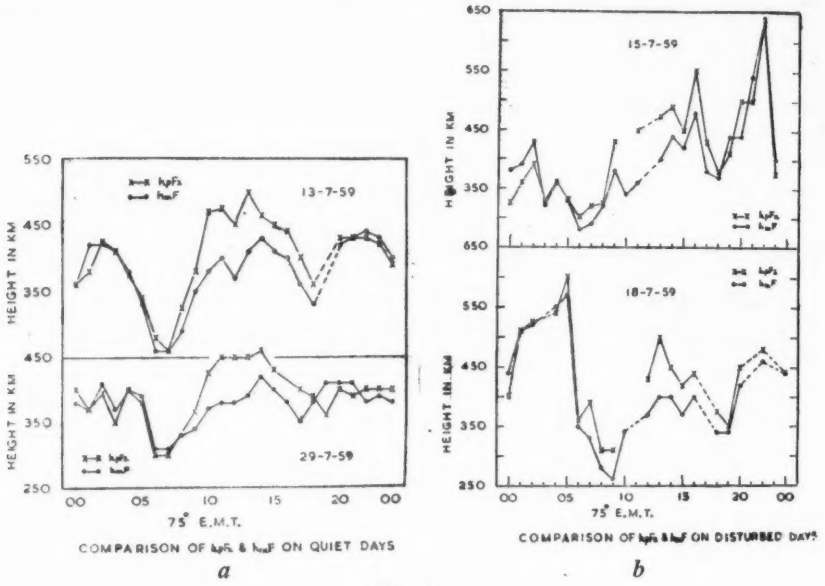


FIG. 4.

between h_pF$_2$ and h_mF is not great at night hours, but during daytime h_mF is lower by 50–60 km. than h_pF$_2$. It may be remembered that h_pF$_2$ is based on the assumption of a parabolic model taking the actual height to be the virtual height at 0·834 of the critical frequency of the F$_2$ layer.

SUMMARY

The paper discusses the results of calculation of electron density—height profiles of the ionosphere in a highly disturbed period in July 1959 from the vertical soundings made at Ahmedabad. After a brief account of the method

of calculation (following Schmerling and Thomas), tables of coefficients for calculating the true heights from the *h'-f* curves of Ahmedabad are given. Charts of equal electron density at intervals of 2×10^5 electrons/c.c. are presented for each day during the period 10 to 19 July.

An appendix is added giving the hourly values of maximum electron density NmF and total electron content n_T for all the days.

Acknowledgements

A good amount of preliminary work required for calculating electron density profiles was done by Dr. S. R. Sreenivasan. The thanks of the author are due to him for making available his working papers and thesis.

The author also wishes to express his thanks to Prof. K. R. Ramanathan under whose guidance the present study was carried out.

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APPENDIX—*July* 1959

Time \ Day	10		11		12		13		14	
E.M.T. 75°	N_m	n_T	N_m	n_T	N_m	n_T	N_m	n_T	N_m	n_T
0	59	47	68	55	75	28	70	28	61	31
1	..	..	..	37	60	53	61	53	61	33
2	..	..	61	44	58	32	52	32	52	38
3	61	49	66	53	58	32	56	32	55	38
4	48	48	75	42	58	28	52	28	..	..
5	61	59	65	57	89	34	51	34	37	30
6	88	41	79	..	..	38	74	38	64	47
7	116	61	85	61	84	56	92	56	114	83
8	..	..	72	118	116	94	100	94	85	79
9	..	..	85	70	83	143	105	143	..	..
10	..	..	104	163	90	170	112	170	..	..
11	..	..	..	172	127	213	164	213	179	235
12	..	..	140	212	194	219	170	219	164	207
13	206	232	..	272	226	272	194	272	179	224
14	215	279	226	207	194	297	226	297	216	275
15	226	269	243	253	210	285	261	285	..	..
16	194	191	216	234	243	282	298	282	279	283
17	179	192	223	222	279	249	314	248	287	211
18	159	119	..	..	..	180	272	180	261	152
19	134	90	194	172	261	..	..	..	..	..
20	96	85	150	155	194	86	115	86	137	118
21	64	47	..	100	124	24	56	24	59	22
22	74	47	81	76	107	39	72	39	70	49
23	74	54	81	62	92	42	72	42	64	53

N_mF in 10^4 electrons/c.c.
n_T in 10^{11} electrons/cm.^{2} col.

APPENDIX—*July* 1959 (*Contd.*)

Time \ Day	15		16		17		18		19	
E.M.T.	N_m	n_T	N_m	n_T	N_m	n_T	N_m	n_T	N_m	n_T
0	70	50	..	..	147	91	98	79	127	84
1	63	43	15	13	140	62	25	27	100	61
2	79	63	..	..	100	67	46	35	90	47
3	64	18	15	14	90	61	..	..	..	..
4	61	43	25	12	79	60	32	23	70	34
5	61	44	20	21	61	14	16	19	61	36
6	62	43	45	62	79	79	21	30	81	63
7	96	70	100	79	121	141	88	91	100	107
8	103	112	114	136	179	114	150	96	150	129
9	137	195	150	163	100	81	84	68	194	168
10	147	175	179	216	137	254	79	125	164	193
11	164	201	179	317	194	268	..	..	179	266
12	..	..	..	..	261	352	164	208	210	221
13	194	249	226	318	243	319	179	210	279	327
14	243	330	..	..	243	340	254	295	279	295
15	261	315	261	276	261	333	279	272	202	275
16	206	304	243	251	261	231	299	277	294	240
17	279	230	226	248	..	..	..	..	..	..
18	243	230	279	279	279	187	317	225	279	210
19	164	240	298	275	143	164	261	214	210	172
20	100	103	243	213	150	127	150	114	164	119
21	88	92	210	122	137	101	..	..	150	116
22	27	16	194	146	124	115	134	91	124	86
23	49	33	137	73	124	109	..	..	..	..

N_mF in 10^4 electrons/c.c.
n_T in 10^{11} electrons/cm.^{2} col.

KINETIC STUDIES IN ESTER HYDROLYSIS

Part XI. The Alkaline Hydrolysis of Some Cinnamic Esters in Mixed Solvents

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INTRODUCTION

IN Part X of this series we reported the results of studies on the esters of benzoic acid and substituted benzoic acids. In analysing the influence of substituents and solvents, it was considered worthwhile to study the corresponding esters of cinnamic acid. The derivatives of the trans acid are easily obtained and they have been used in the present study.

EXPERIMENTAL

The esters and the solvents were purified by standard methods. The physical constants of the esters are given below.

Ethyl Cinnamate	.. b.p. 271·0° C. n^{30}_D 1·5530	Dipole moment. 1·84
2 Nitro-Ethyl Cinnamate	.. m.p. 44·0° C.	4·94*
4-Nitro-Ethyl Cinnamate	.. m.p. 141·8° C.	3·50
Benzyl Cinnamate	.. m.p. 39·0° C.	1·97*

Rate studies were as in earlier parts. Consistent second-order rate constants were obtained in all cases.

DISCUSSION

It was found from preliminary studies that the range of solvent compositions that could be used for homogeneous conditions was small and isocomposition data could be conveniently used for comparisons. The graph of $\log_{10} k$ against 1/T gave a good linear relation. The rate constants and other relevant data are presented in Tables I and II.

* These dipole moments were determined by Mr. T. Devanathan in these laboratories.

TABLE I

Rate constants in the alkaline hydrolysis in dioxan water and acetone-water systems [*Moles*$^{-1}$ *Sec.*$^{-1}$]

Ester	Solvent composition % Organic component	Temperature ° C.		
		30	35	40
Ethyl Cinnamate ..	50% Dioxan	0·01430	0·02010	0·02780
..	60% „	0·01160	0·01660	0·02340
..	70% „	0·01020	0·01479	0·02110
..	50% Acetone	0·01225	0·01790	0·02580
..	60% „	0·00900	0·01330	0·01936
..	70% „	0·00752	0·01125	0·01670
Benzyl Cinnamate ..	50% Dioxan	0·02300	0·03260	0·04337
..	60% „	0·02001	0·02812	0·03890
..	70% „	0·01670	0·02270	0·03350
..	50% Acetone	0·01780	0·02580	0·03666
..	60% „	0·01530	0·02243	0·03250
..	70% „	0·01130	0·01687	0·02450
2-Nitro-Ethyl Cinnamate ..	50% Acetone		0·1539	0·2164
..	60% „		0·1153	0·1648
..	60% „		0·0999	0·1446
4-Nitro Ethyl Cinnamate ..	50% Acetone		0·1657	0·2164
..	60% „		0·1226	0·1742
..	70% „		0·1242	0·1503

In general, the trends in the different parameters conform to earlier observations. On the basis of the collision theory one expects a pre-exponential factor of the order of 10^{11} and all the values are consistently lower. Several factors contribute to this lowering:

TABLE II

Arrhenius parameters and thermodynamic constants

Ester	Solvent composition	△E	⊿H	$\log_{10}PZ$	△S
Ethyl Cinnamate ..	50% Dioxan	12530	11917·8	6·7892	−27·55
	60% „	13220	12607·8	7·59	−23·89
	70% „	13710	13097·8	7·89	−21·5
	50% Acetone	14040	13427·8	8·2089	−21·05
	60% „	14440	13827·8	8·36	−20·34
	70% „	15040	14427·8	8·73	−18·16
Benzyl Cinnamate ..	50% Dioxan	11560	11347·8	6·99	−26·61
..	60% „	12530	11917·8	7·35	−25·11
..	70% „	13120	12507·8	7·67	−23·47
..	50% Acetone	13610	12997·8	8·26	−20·81
..	60% „	14200	13587·8	8·4208	−20·08
..	70% „	14580	13567·8	8·56	−19·41
p-Nitro-Ethyl Cinnamate	50% Acetone	12940	12327·8	8·39	−20·18
..	60% „	13460	12847·8	8·63	−19·11
..	70% „	14040	13427·8	8·97	−17·07
O-Nitro Cinnamate ..	50% Acetone	13070	12457·8	8·45	−19·92
..	60% „	13690	13077·8	8·77	−18·47
..	70% „	14170	13557·8	9·04	−17·20

(i) The formation of the activated complex can be endothermic.

(ii) The reaction may involve the prior ionisation of the dipolar component.

(iii) Solvent molecules may deactivate part of the reactants.

(iv) Stringent conditions of orientation may be present,

(v) The repulsive forces may be appreciable,

In the olefine bromine reaction, it has been shown[1] that taking into account the geometry of the reactants and the topology of the transition state, part of the low pre-exponential values could be accounted for. Applying the same approach Nair[2] has shown that this orientation factor largely accounts for these lowered values in ester hydrolysis as well.

The Arrhenius activation energy as well as the thermodynamic constants give us clear indications of the influence of structure. With the same solvent composition, the values of activation energies appear to be nearly as those of the corresponding benzoates within the limits of experimental error.[2a] The introduction of a double bond between the reacting zone and the substituent makes no appreciable difference to the electrostatic forces. However, the small consistent increase in all solvent compositions shows that the result of such an interposition is not negligible. The two series show similar values of the pre-exponential term so that one has to account for the faster reaction in the case of the cinnamates.

The esters of benzoic and cinnamic acids differ from the aliphatic analogues in requiring an extra-activation energy to overcome the resonance energy in the formation of the transition state.[3] The rates in both series should be slower as is observed. A comparison of the Hammett constant also shows that the two series are analogous.

TABLE III

50% *Dioxan*

Ester	K_2 at 40°	log K	σ	ρ
Ethyl acetate ..	·1601	$\bar{1}$. 2044	·00	1·00
Ethyl benzoate ..	·0145	$\bar{1}$. 1614	−1·06	1·00
Ethyl cinnamate ..	·0278	$\bar{1}$. 4440	−0·75	1·00

Calculation of the rate constant from the ρ and σ values gives a value very close to the observed one.

A change in the alkyl part of the molecule is not without effect though the replacement of ethyl by benzyl is insufficient to alter the mechanism of fission. Substituents in the aryl part are more effective in altering the parameters and significantly it will be observed that there is very litle difference between a nitro group in the *ortho*- and *para*-positions. This contrasts with the benzoates where the pre-exponential factor and the entropy of activation

both show large differences though the activation energies do not differ appreciably. The differences between the two series thus indicate that, in the overall picture, repulsive forces have to be reckoned with, the magnitude of which is a contributory factor in the alternation of the reaction rate. It is also to be expected that an *ortho*-substituent is more effective in its contribution to repulsive forces in the benzoate series.

Turning to solvent influences, again we notice the sharp difference between acetone and dioxan solutions. Where both solvents have been studied, acetone-water solutions invariably show a larger activation energy. It has been indicated in Part X that part of the difference can be attributed to the structure-breaking effect of acetone. Our earlier studies[4] have also indicated some abnormalities in the region of small additions of organic solvent. All the observations lead to the conclusion that even in these reactions where water is a reactant at some stage or other, while some correlation with water content should be present other factors enter.

SUMMARY

In continuation of our studies on ester hydrolysis, the kinetic studies of cinnamates are reported. A close correlation between benzoates previously reported and cinnamates is noticed. The differences in the reactivity of these esters are explained.

ACKNOWLEDGMENT

The author wishes to express his thanks to Prof. S. V. Anantakrishnan, Chairman, Department of Chemistry, Madras Christian College, for his guidance throughout the course of this work.

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DIPOLE MOMENTS AND MOLECULAR STRUCTURE OF PICRATES OF AROMATIC HYDROCARBONS AND HETEROCYCLIC AMINES

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Introduction

A great number of typical molecular compounds belong to the group of complexes formed of molecules, in the formation of which no atoms are transferred but in a certain measure a transfer of electrons takes place. Such compounds with different donor acceptor types in which the original molecules associate in a definite ratio have been described in a classical review by Pfeiffer[24] and in recent literature.[3, 13, 33] Considerable attention has been given to various physical methods which have been successfully applied to show the existence and to study their properties like equilibrium constants,[16, 26] heats of formation and other thermochemical data,[3,4] melting point elevation,[27] magnetic susceptibilities,[12] optical constants,[21] viscosity[3] and X-ray, infra-red, etc., data.[8, 11] Information regarding the nature of the binding forces in such compounds as derived from a study of electric polarization and dipole moments have also been recorded.[3, 6, 14, 15, 28, 30]

A large number of hydrocarbon, ether, phenol, amine oxide, and other closely related derivatives of polynitro-compounds can be obtained in crystalline form and belong to the class of non-salt-like compounds. The polynitro-compound complexes have been the subject of many investigations.[2, 7, 18, 25, 32] However, these have not brought any fundamental clarification of the physical origin of the absorption bands characteristic of these molecular complexes.[19, 20, 22] Though the possibility of a clarification of the binding in molecular compounds under the assumption of an electron transfer mechanism between the donor and acceptor components of the molecular complex has been put forth by various authors[5, 31] the quantum mechanical quantitative formulation was due to Mulliken.[19, 20] Dipole moment measurements have been made in the case of a few aromatic hydrocarbon picrates and discussed in terms of the integrated theory of Mulliken.

Measurements have also been extended to include a few salt-like heterocyclic amine picrates.

EXPERIMENTAL

Materials and Their Purification

Aromatic hydrocarbon picrates.—Naphthalene and acenaphthene picrates were obtained from alcoholic solutions, while phenanthrene picrate from benzene solution. All three picrates were recrystallised from ethyl alcohol.

Naphthalene picrate: Yellow needles, melting point 149° C.

Acenaphthene picrate: Orange needles, melting point 162° C.

Phenanthrene picrate: Orange brown needles, melting point 162° C.

Heterocyclic amine picrates.—All the heterocyclic amines were used in alcoholic solutions.

Pyridine picrate, recrystallised from alcohol thrice, melting point 164° C.

Piperidine picrate, recrystallised from water and dried *in vacuo*. Yellow stout needles, melting point 151° C.

α-Picoline picrate, recrystallised from water and dried *in vacuo*. Yellow stout crystals, melting point 169° C.

β- and γ-Picoline picrates—Both recrystallised from alcohol. Puffy needles, melting points 170° C. and 168° C. respectively.

Quinoline picrate, recrystallised from dioxan, melting point 202° C.

Isoquinoline picrate, recrystallised from large volume of alcohol, yellowish needles, melting point 221° C.

Apparatus and Methods of Measurement

Details of the apparatus and methods of measurement of dielectric constants and densities have been given in an earlier paper.[29] The same procedure has been adopted for the evaluation of dipole moments.

DISCUSSION

Aromatic hydrocarbon picrates.—Mulliken has classified the hydrocarbon picrates as belonging to the neutral even system containing easily ionized bonding π electrons ($b\ \pi_a$) *plus* neutral even system containing relatively strongly held π electrons ($x\ \pi_a$) type. Evidence for characterising these as

TABLE I

Temperature 35° ± 0·01° C. Solvent: Dioxan

Mole fraction	Dielectric constant	Density
	Naphthalene picrate	
0·001112	2·20818	1·01805
0·002699	2·22146	1·01980
0·004200	2·23143	1·02150
0·004609	2·33540	1·02199
0·003818	2·22871	1·02122
	Acenaphthene picrate	
0·001321	2·20661	1·01840
0·003126	2·22143	1·02067
0·001889	2·21085	1·01908
0·001914	2·21145	1·01911
	Phenanthrene picrate	
0·000398	2·19603	1·01732
0·000551	2·19754	1·01751
0·001578	2·21115	1·01889
0·001615	2·21175	1·01893
	Pyridine picrate	
0·000158	2·21965	1·01805
0·000396	2·24255	1·01832
0·000560	2·26147	1·01857
0·001115	2·31822	1·01926
0·001765	2·39289	1·02000
	Piperidine picrate	
0·001216	2·37994	1·01934
0·001970	2·45661	1·02006
0·003625	2·62686	1·02198
0·004998	2·75330	1·02350

TABLE I (*Contd.*)

Mole fraction	Dielectric constant	Density
	α-Picoline picrate	
0·000039	2·22156	1·01878
0·000282	2·25000	1·01910
0·000607	2·28742	1·01958
0·000789	2·31138	1·01983
0·001115	2·34930	1·02030
	β-Picoline picrate	
0·000113	2·22255	1·01904
0·000200	2·23300	1·01914
0·000591	2·28360	1·01961
0·000800	2·31138	1·01986
	γ-Picoline picrate	
0·000101	2·22958	1·01723
0·000273	2·25156	1·01743
0·000509	2·28156	1·01780
0·000941	2·33654	1·01833
	Quinoline picrate	
0·000059	2·20296	1·01690
0·000130	2·20931	1·01698
0·000217	2·21687	1·01708
0·000070	2·20386	1·01692
	Iso-quinoline picrate	
0·000031	2·22458	1·01720
0·000108	2·23160	1·01730
0·000150	2·23658	1·01736
0·000262	2·24657	1·01750

TABLE II

	Naphthalene picrate	Acenaphthene picrate	Phenanthrene picrate
Hedestrand α ..	3·28	3·62	6·04
Hedestrand β ..	1·125	1·18	1·246
Molar refraction (cm.^{3})* ..	88·48	95·66	103·96
Total polarisation (cm.^{3}) ..	182·34	195·52	278·91
Orientation polarisation (cm.^{3}) ..	93·86	99·86	174·95
Dipole moment (D) ..	2·18	2·25	2·97

* Calculated from bond refractions given by Denbigh (*see* Ref. 29).

members of the above type is due to the fact that a strong charge-transfer absorption maximum is observed in the case of naphthalene picrate.[26] The following assumptions are made in the application of the charge transfer scheme of Mulliken: (i) The molecular components try to combine so that the polarization and dispersion forces are possibly large and consequently the planar rings of picric acid and the hydrocarbon must lie parallel with mutual approximately symmetrical axis passing through the plane of the rings. (ii) The charge transfer co-ordinate does not much deviate from the line perpendicular to the two rings. (iii) The interplanar distance has been assumed to be 3·2 Å as has been fixed by Briegleb and Czekalla[6] for the chloranil hexamethyl benzene complex. (iv) The ionic character has been calculated assuming that the component of the moment of picric acid along the charge transfer co-ordinate is small and hence neglected.

According to the theory of Mulliken, from the known values of S, μ_1 (the ionic moment), μ_0 (the covalent moment) and μ_N (experimental moment), the coefficients a and b as well as the ratio $b^2/(a^2 + b^2)$ corresponding to the ionic character has been calculated and recorded in Table IV.

The $b\ \pi_a + x\ \pi_a$ complexes of aromatic hydrocarbons with polynitro-compounds like picric acid involve partially localised donor-acceptor interaction similar to that postulated by Abrahams.[1] In fact for such 1 : 1 complexes between aromatic or unsaturated π donor and π acceptors of the aromatic polynitro-compound type, Mulliken's theory predicts that the electric vector should be polarised with a large component perpendicular to the

TABLE III

	Pyridine picrate	Piperidine picrate	α-Picoline picrate	β-Picoline picrate	γ-Picoline picrate	Quinoline picrate	Isoquinoline picrate
Hedestrand α ..	46·31	45·51	52·89	56·16	56·77	40·88	42·56
Hedestrand β ..	1·238	1·114	1·362	1·130	1·251	1·112	1·253
Molar refraction ($cm.^3$)*	72·75	75·11	77·40	77·40	77·40	88·29	88·29
Total polarisation ($cm.^3$)	1568·75	1534·38	1768·16	1879·44	1898·29	1329·36	1449·27
Orientation polarisation ($cm.^3$)	1496·00	1459·27	1690·76	1802·04	1820·89	1241·07	1360·98
Dipole moment (D) ..	8·70	8·59	9·25	9·55	9·60	7·92	8·30

* Calculated from bond refractions of Denbigh (*see* Reference 29).

TABLE IV*

Molecular compound	Moment of the hydrocarbon	Moment of the complex	a	b†	$b^2/(a^2+b^2)$
Naphthalene picrate ..	0·00	2·18	0·9109	0·3304	0·117
Acenaphthene picrate	0·97	2·25	0·9039	0·3362	0·122
Phenanthrene picrate ..	0·00	2·97	0·8811	0·39380	0·166

* The value of overlap integral S is taken to be 0·1 as assumed by Mulliken.
$\mu_1 = e \times 3{\cdot}2$ Å $= 15{\cdot}3$ D and $\mu_0 = 0$.

† Mainly because of its strong dependence on the uncertain quantity S the value of b can only be relative.

TABLE V*

Picrate	Moment of the base	Covalent moment μ_0	Moment of the complex	a	b†	$b^2/(a^2+b^2)$
Pyridine ..	2·21	2·257	8·70	0·7036	0·6982	0·496
Piperidine ..	1·17	1·625	8·59	0·6920	0·7092	0·512
α-Picoline ..	1·72	1·914	9·25	0·6644	0·7355	0·551
β-Picoline ..	2·30	2·325	9·55	0·6584	0·7411	0·559
γ-Picoline ..	2·57	2·539	9·60	0·6609	0·7389	0·556
Quinoline ..	2·18	2·235	7·92	0·7434	0·6557	0·438
Isoquinoline ..	2·52	2·498	8·30	0·7316	0·6686	0·455

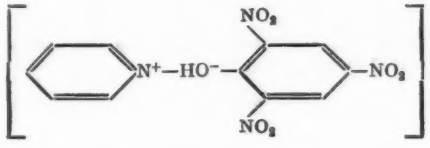
* Resultant of picric acid 1·57 D[17] was taken as acting at an angle of 71° to the C–O bond. This angle was derived from the bond moment values of 0·8 D for the C–O link and 1·51 D for the H–O link, from which and a resultant moment of 1·51 D, an angle of 101° was obtained for the CÔH. In all the heterocyclic amines the resultant moments were assumed to act from nitrogen towards the ring[22]. R_{ab} employed in the above calculations was taken from N–O distance in hydroxylamine hydrochloride.[10]

$\mu_1 = 4{\cdot}803 \times 3{\cdot}22$ Å $= 15{\cdot}46$ D. S = 0·0177 calculated from S_{ab} Staler overlap integral using Slater μ values for N^+O^- ions.[21]

† Mainly because of its strong dependence on the uncertain quantity S the value of b can only be relative.

planes of the two interacting molecules which are parallel to each other. In such cases of closed shell donors and acceptors, when a donor and the acceptor come into close proximity, the initial no-bond function ψ_0 (D.A) becomes increasingly admixed with a dative function ψ (D^+A^-). Though ψ_0 would result in a steady rise in exchange repulsion for increasingly close approach[19, 20] a charge transfer outer complex can be formed, the corresponding repulsion energy rise being overcome by resonance between ψ_0 and ψ_1.

Heterocyclic amine picrates.—In the following structure given for the ionic but indissociated reaction product



C will be only slightly larger than zero. If C is increased the hydrogen atom moves towards the nitrogen with the consequent tendency for Sp^3 hybridization. In the ultimate analysis, the U (C) curves for the complexes of the heterocyclic amine picrate type ($n + h\sigma_d$), should probably have a shallow minimum showing an inner complex corresponding to ($C = 1$), $b^2 \approx a^2$ and an activated complex ($C=0{\cdot}5$) (Table V). The variation of ionic character values $b^2/(a^2 + b^2)$ from 0·559 for β-picoline picrate to 0·438 for quinoline picrate shows that the structure of the picrates varies in between an inner complex with maximum transfer and an activated complex, the individual salt molecules being stable in dioxan solutions.

SUMMARY

Dipole moment measurements have been made in the case of a few aromatic hydrocarbon picrates, the values obtained being 2·18, 2·25, 2·97 (all in Debye units) for picrates of naphthalene, acenaphthene and phenanthrene respectively and the results discussed in terms of Mulliken's theory. Measurements have also been extended to include a few salt-like heterocyclic amine picrates.

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ANTHOXANTHIN PIGMENTS OF THE LEAVES OF *DIGITALIS LANATA* EHRH. AND THE CONSTITUTION OF A NEW PIGMENT DINATIN

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The occurrence of luteolin in the leaves of *Digitalis purpurea* was reported long time back.[1] The 7-glucoside of luteolin has also been found to occur in the same plant.[2] Digitolutein, a new yellow pigment of *D. lutea*[3] and *D. purpurea*,[4] has been shown to be the 3-methyl alizarin 1-methyl ether.[5,6] In the course of work on the preparation of digitoxin from the leaves of a Spanish *Digitalis* of uncertain botanical identity but considered to be very probably *D. thapsi*, Karrer[7] reported the isolation of a flavone pigment thapsin which was subsequently found[8] to be identical with calycopterin isolated from the leaves of *Calycopteris floribunda*.[9]

In the course of our work on the commercial *D. lanata* leaves grown in Kashmir for cardioactive principles we found that the drug contains an appreciable quantity of flavone pigments. The present paper deals with the chemical examination of the pigments isolated from this material.

The powdered leaves were extracted with alochol in the cold. From the concentrate after removal of lipoid material with petroleum ether and benzene the pigments were extracted with ether. Two fractions 1 and 2 were obtained, both of which were yellow in colour and answered colour reactions for anthoxanthins.

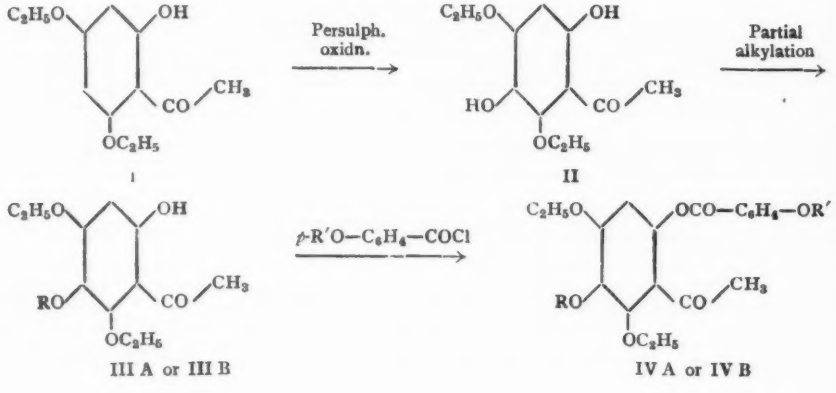
Fraction 1 could not be completely purified by mere fractional crystallization; however, fractional crystallization of the mixed acetate yielded two pure entities which were deacetylated to recover the original compounds. The properties and composition of the two acetates and their deacetylated products indicated that the substances in question were scutellarein (5 : 6 : 7 : 4′-tetrahydroxy flavone) and luteolin (5 : 6 : 3′ : 4′-tetrahydroxy flavone). The identity of scutellarein which has no recognizable m.p. was confirmed by the preparation of its tetramethyl ether (this ether was also needed to settle the constitution of dinatin, *see* later).

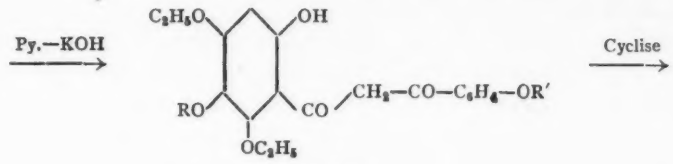
Purification of fraction 2 yielded a compound, m.p. 274–76°. It answered anthoxanthin colour reactions, analysed for the formula $C_{16}H_{12}O_6$ with one methoxyl and formed a triacetate. Its complete methyl ether was found

to be identical with scutellarein tetramethyl ether and its demethylation product with scutellarein. Thus the pigment seems to be a monomethyl ether of scutellarein not described in the literature so far and is therefore designated as dinatin. The pigment was soluble in aqueous sodium carbonate solution indicating a free 7-hydroxy group. Of the three remaining positions for the methoxyl the 4′ and 6 positions have a greater probability than the 5, since the 5-hydroxyl group in anthoxanthins is known to be relatively hindered. The first possibility (4′-position) for the methoxyl can easily be settled if on alkaline degradation anisic acid and/or *p*-methoxyacetophenone can be identified among the products. This approach however was ruled out as not enough material was available for a fission experiment. Hence recourse was had to the following synthetic approach. The compound dinatin was fully alkylated using ethyl sulphate and the complete mixed ether compared directly with synthetic specimens of 5:6:7-triethoxy-4′-methoxyflavone and 5:7:4′-triethoxy-6-methoxyflavone. The triethyl ether of dinatin was found to be identical with the former but not with the latter, indicating that dinatin is 4′-O-methyl scutellarein (VII). This structure for dinatin agrees with the observation that it gives a positive Bargellini[10] test which is considered to be characteristic of flavones and flavonols having hydroxyl groups in the 5:6:7-positions.

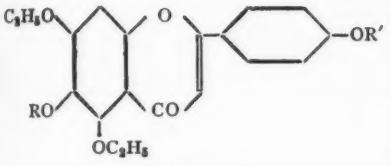
The synthetic triethoxy-monomethoxy compounds mentioned above and which are not described in the literature were prepared from phloracetophenone diethyl ether along the lines described by Sastri and Seshadri,[11] except that the rearrangement of the substituted benzoyloxy compound to the diketone has been accomplished by the method of Gallagher *et al.*[12] The sequence of reactions is shown in Chart 1.

CHART 1

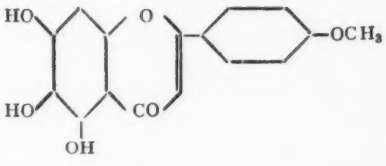




V A or V B



VI A or VI B



VII

In formulæ III—VI

R = CC_2H_5 and R′ = OCH_3 in the A series

and R = OCH_3 and R′ = OC_2H_5 in the B series

Experimental

Note.—The alkoxyl content of mixed ethers described herein are calculated and expressed as ethoxyl.

The powdered leaves (3 kg.) were extracted with 90% alcohol (4×6 litres) in the cold. The combined extracts were concentrated under reduced pressure to 800 ml. and extracted in succession with petroleum ether (5× 500 ml.), benzene (5×500 ml.) and ether (6×400 ml.). After these extractions the concentrate was almost devoid of anthoxanthin pigments (magnesium-hydrochloric acid reaction). All the extracts were washed with water and dried over sodium sulphate.

The petroleum ether extract (32 g.) and the benzene extract (41 g.) were dark-greenish-brown amorphous semi-solids and were not examined further.

Ether extract.—The bulk of the solvent was removed by distillation and the concentrate was set aside for three days when a yellow solid separated (fraction 1, 2·8 g.). It was filtered and washed with petroleum ether followed by ether. The filtrate was further concentrated and set aside for a number of days when some more yellow solid separated (fraction 2, 0·8 g.). The mother liquors of fraction 2 did not yield any more solid.

Fraction 1.—This gave a red colour with magnesium and hydrochloric acid. With lead acetate in alcohol solution it gave an yellow precipitate. It was soluble in aqueous sodium hydroxide and sodium carbonate solutions.

With alcoholic ferric chloride it gave a deep-brown colour. The solid melted indefinitely between 270° and 300°. Repeated fractional crystallizations from the common organic solvents did not yield wholly satisfactory results. The material (2 g.) was acetylated by heating under reflux with anhydrous sodium acetate (4 g.) and acetic anhydride (5 ml.) at 130–40° for 4 hours. The crude acetate (2·2 g.) after an initial crystallization from benzene-petroleum ether was fractionally crystallized from acetone. The less soluble fractions were combined and crystallized twice from alcohol-acetone when long silky needles were obtained, m.p. 238–40° (acetate A) (1·2 g.).

The more soluble fractions after repeated crystallizations from alcohol gave colourless needles, m.p. 215–17° (acetate B) (0·4 g.).

Characterization of acetates A and B

Acetate A, m.p. 238–40°.—On magnesium-hydrochloric acid reduction it gave an orange-red colour. With alcoholic ferric chloride no colour was obtained. Found: C, 60·4; H, 4·3; $-COCH_3$, 38·6%. $C_{23}H_{18}O_{10}$ (Scutellarein tetraacetate) requires: C, 60·8; H, 4·0; $-COCH_3$ (4), 37·9%.

Deacetylation of A to scutellarein.—A solution of the substance (300 mg.) in alcohol (20 ml.) and acetone (4 ml.) was refluxed with 1 N sulphuric acid (100 ml.) for 10 hours in a water-bath. The organic solvents were removed under reduced pressure and the aqueous residue cooled, when an yellow solid separated out, which was filtered, washed with water and dried (yield 180 mg.). It crystallized from methanol as yellow leaflets. It did not melt below 340° but decomposed above 350°. It gave a red colour on reduction with magnesium-hydrochloric acid, an yellow precipitate with lead acetate and a reddish-brown colour with alcoholic ferric chloride. It formed an yellow solution with aqueous sodium hydroxide and sodium carbonate solutions which immediately turned green. Found: C, 63·4; H, 3·8%. $C_{15}H_{10}O_6$ (scutellarein) requires: C, 63·0; H, 3·5%.

Methylation of scutellarein.—A solution of the substance (80 mg.) in anhydrous acetone (15 ml.) was refluxed for 30 hours with dimethyl sulphate (1 ml.) and anhydrous potassium carbonate (2 g.). The product was crystallized from acetone-petroleum ether and then from alcohol when colourless prisms were obtained, m.p. 156–58°. It gave no colour with ferric chloride. Found: C, 67·1; H, 4·9; $-OCH_3$, 34·8%. $C_{19}H_{18}O_6$ (scutellarein tetramethyl ether) requires: C, 66·7; H, 5·3; $-OCH_3$ (4), 36·2%.

Acetate B, m.p. 215–17°.—This substance gave an orange-red colour on reduction with magnesium-hydrochloric acid but gave no colour with ferric chloride. Found: C, 60·2; H, 4·5; $-COCH_3$, 38·6%. $C_{23}H_{18}O_{10}$

(luteolin tetraacetate) requires: C, 60·8; H, 4·0; $-COCH_3$ (4), 37·9%.

Deacetylation of B to luteolin.—The substance (0·3 g.) was dissolved in alcohol (25 ml.), treated with 1 N sulphuric acid (100 ml.) and the mixture refluxed for 10 hours in a water-bath. The yellow solid that separated out on working up the product was filtered, washed with water and dried (yield 160 mg.). It crystallized from alcohol as yellow needles, m.p. 334–38°. It gave an orange-red colour on reduction with magnesium-hydrochloric acid, a yellow precipitate with lead acetate and a greenish-brown colour with ferric chloride. Found: C, 62·8; H, 3·9%. $C_{15}H_{10}O_6$ (luteolin) requires C, 63·0; H, 3·5%.

Fraction 2.—Repeated fractional crystallizations from alcohol rejecting each time the less soluble portion gave pale-yellow needles, m.p. 274–76° (dinatin, yield 0·5 g.). It was soluble in sodium hydroxide and sodium carbonate solutions, gave an orange-red colour with magnesium-hydrochloric acid, yellow precipitate with lead acetate and dark-brown colour with ferric chloride. Bargellini test was positive. Found: C, 63·6; H, 4·5; $-OCH_3$, 10·4%. $C_{16}H_{12}O_6$ requires: C, 64·0; H, 4·0; $-OCH_3$ (1), 10·3%.

Dinatin triacetate.—Dinatin (100 mg.) was acelytated with anhydrous sodium acetate and acetic anhydride and the product crystallized twice from benzene-petroleum ether and once from ethyl acetate when it was obtained as prismatic needles, m.p. 168–70° (yield 70 mg.). It gave no colour with ferric chloride. Found: C, 62·5; H, 4·7; $-OCH_3$, 7·0; $-COCH_3$, 31·2%. $C_{22}H_{18}O_9$ (triacetate) requires: C, 62·0; H, 4·3; $-OCH_3$ (1), 7·3; $-COCH_3$ (3) 30·3%.

Methyl ether of dinatin.—The substance (100 mg.) was dissolved in dry acetone (15 ml.) and to the solution anhydrous potassium carbonate (2 g.) and dimethyl sulphate (1 ml.) were added and the mixture was refluxed for 30 hours. The product was crystallized from alcohol (charcoal) when colourless prisms, m.p. 158–60°, were obtained (40 mg.). The substance gave no colour with ferric chloride. Found: C, 67·0; H, 5·8; $-OCH_3$, 35·3%. $C_{19}H_{18}O_6$ (scutellarein tetramethyl ether) requires: C, 66·7; H, 5·3; $-OCH_3$ (4), 36·2%. Mixed m.p. with tetramethyl scutellarein (*see* above) was undepressed (156–58°).

Demethylation of dinatin.—The substance (100 mg.) was dissolved in glacial acetic acid (2 ml.) and treated with a saturated solution of hydrobromic acid in glacial acetic acid (4 ml.) and the mixture was heated in a boiling

water-bath for 2 hours. The product crystallized from alcohol as small yellow leaflets which did not melt below 340°. The substance answered all the colour reactions described above under scutellarein. Found: C, 62·6; H, 3·9; $-OCH_3$, nil. $C_{15}H_{10}O_6$ (scutellarein) requires: C, 63·0; H, 3·5%.

Triethyl ether of dinatin.—Dinatin (70 mg.) was dissolved in acetone (12 ml.) and to the solution anhydrous potassium carbonate (2 g.) and diethyl sulphate (0·8 ml.) were added and the mixture was refluxed for 48 hours. The product was twice crystallized from acetone-petroleum ether when colourless needles were obtained, m.p. 144–46°. Found: C, 68·4; H, 6·7 $-OC_2H_5$, 45·9%. $C_{22}H_{24}O_6$ requires: C, 68·7; H, 6·3; $-OC_2H_5$ (4), 46·9%.

Synthesis of 5:6:7-*Triethoxy*-4′-*Methoxy Flavone*

2: 5-*Dihydroxy*-4: 6-*diethoxy acetophenone* (*II*).—2-Hydroxy-4 : 6-diethoxy acetophenone[13] (I), m.p. 84–85° (2 g.), was treated with pyridine (20 ml.) and potassium hydroxide (5 g.) in water (30 ml.) and the solution cooled to a temperature of 15–20° and kept continuously stirred. A solution of potassium persulphate (2·5 g.) in water (50 ml.) was then introduced dropwise during the course of 4 hours, the temperature being maintained at 15–20° throughout the reaction. After allowing to stand for 24 hours the reaction mixture was rendered acid to congo-red by the addition of conc. hydrochloric acid. The unreacted original ketone which separated was filtered and washed with a small quantity of water. The combined aqueous filtrate and washings were treated with sodium sulphite (1g.), conc. hydrochloric acid (35 ml.) was then added and the solution heated at 85–90° in a water-bath for 30 minutes. On cooling it rapidly deposited a brownish-yellow crystalline material which was filtered, washed with water and dried, m.p. 120–23° (yield 0·9 g.). It crystallized from alcohol as yellow prisms, m.p. 125–26° and gave the characteristic colour reactions of *p*-dihydroxy phenols.[11] Found: C, 60·5; H, 7·0; $-OC_2H_5$, 36·7%. $C_{12}H_{16}O_5$ requires: C, 60·0; H, 6·7%; $-OC_2H_5$ (2), 37·5%.

2-*Hydroxy*-4: 5: 6-*triethoxy acetophenone* (*III A*).—The 2: 5-dihydroxy compound (650 mg.) was dissolved in acetone (10 ml.) and benzene (40 ml.) and treated with anhydrous potassium carbonate (1·5 g.) and diethyl sulphate (0·4 ml.; 1·1 mole) and the mixture refluxed in a water-bath for 12 hours. The inorganic salts were filtered and washed with hot benzene. The filtrate and washings were washed with 5% aq. sodium carbonate and water, dried over sodium sulphate and the solvent removed under vacuum. The reddish-brown oily residue was taken in ether and diluted with petroleum ether

when the last traces of unchanged dihydroxy compound got precipitated. The clear petroleum ether solution after the removal of solvent gave 2-hydroxy-4:5:6-triethoxy acetophenone as an orange-yellow oil (yield 350 mg.). It gave a deep violet-brown colour with ferric chloride.

2-*Anisoyloxy*-4:5:6-*triethoxy acetophenone* (*IV A*).—2-Hydroxy-4:5:6-triethoxy acetophenone (360 mg.) was anisoylated by heating with freshly distilled anisoyl chloride (0·5 ml.) and dry pyridine (10 ml.) for 2 hours on a boiling water-bath. The reaction mixture was poured into ice-cold water containing hydrochloric acid with stirring. The anisoyl derivative which separated as a semi-solid was taken in ether, the ether solution washed successively with dilute hydrochloric acid, aq. sodium carbonate and water, dried over sodium sulphate and the solvent distilled, when an orange-red semi-solid (0·5 g.) was obtained. Attempts to crystallise it proved unsuccessful. It was insoluble in sodium hydroxide and gave no colour with ferric chloride.

Diketone (*V A*).—The above anisoyl derivative (0·5 g.) was taken in dry pyridine (4 ml.) and freshly powdered potassium hydroxide (0·8 g.) was added to it. The mixture was shaken for 4 hours in a water-bath maintained at 45°, then treated with 20% ice-cold acetic acid (30 ml.) and left in the ice-chest overnight. The crude diketone was crystallized twice from methanol when bright yellow prismatic needles, m.p. 114–16°, were obtained (yield 0·3 g.). It gave a green colour with ferric chloride. Found: C, 64·9; H, 6·9; $-OC_2H_5$, 43·1%. $C_{22}H_{26}O_7$ requires: C, 65·7; H, 6·5; $-OC_2H_5$ (4), 44·8%.

5:6:7-*Triethoxy*-4′-*methoxy flavone* (*VI A*).—A mixture of the above diketone (0·2 g.), glacial acetic acid (3 ml.) and fused sodium acetate (0·5 g.) was gently boiled for 3 hours and diluted with water (20 ml.) when a colourless solid separated. It was filtered, washed with water, dried and crystallized from acetone-petroleum ether and ether-petroleum ether, when colourless needles were obtained, m.p. 146–48° (yield 70 mg.). It gave an orange-red colour with magnesium-hydrochloric acid but gave no colour with ferric chloride. Found: C, 68·4; H, 6·6; $-OC_2H_5$, 44·8%. $C_{22}H_{24}O_6$ requires: C, 68·7; H, 6·3; $-OC_2H_5$ (4), 46·9%. Mixed m.p. between this compound and triethyl dinatin was undepressed (145–47°).

Synthesis of 5:7:4′-*Triethoxy*-6-*Methoxy Flavone.*

2-*Hydroxy*-5-*methoxy*-4:6-*diethoxy acetophenone* (*III B*). 2:5-Dihydroxy-4:6-diethoxy acetophenone (*II*) (350 mg.) was partially methylated using 1·1 mole of dimethyl sulphate. The product was obtained as an

orange-yellow oil (270 mg.) which gave a violet-brown colour with ferric chloride.

2-(p-*Ethoxy benzoyloxy*)-5-*methoxy*-4: 6-*diethoxy acetophenone* (*IV B*).—The above described product (270 mg.) was treated with pyridine (10 ml.) and freshly distilled *p*-ethoxy-benzoyl chloride (0·5 ml.) and the mixture heated under reflux for 3 hours in a water-bath. The product was worked up as described earlier under the anisoyloxy compound. The *p*-ethoxy-benzoyl derivative could be obtained only as semi-solid (yield 300 mg.) which did not dissolve in aq. sodium hydroxide and gave no colour with ferric chloride.

Diketone (*V B*).—The above acyl derivative (300 mg.) was dissolved in dry pyridine (3 ml.) and freshly powdered potassium hydroxide (0·6 g.) was added and the reaction carried out as already described. The crude diketone was crystallized from methanol when bright yellow prismatic needles, m.p. 97–98° (yield 200 mg.), were obtained. The substance gave a green colour with ferric chloride. Found: C, 65·2; H, 6·9; $-OC_2H_5$, 43·4%. $C_{22}H_{26}O_7$ requires: C, 65·7; H, 6·5; $-OC_2H_5$ (4), 44·8%.

5: 7: 4′-*Triethoxy*-6-*methoxy flavone* (*VI B*).—The above diketone(100 mg.) was cyclised by heating with glacial acetic acid and fused sodium acetate for 3 hours and the product crystallized from ether-petroleum ether when colourless needles, m.p. 138–40° (yield 40 mg.) were obtained. The substance gave an orange-red colour with magnesium-hydrochloric acid but gave no colour with ferric chloride. Found: C, 68·3; H, 6·7; $-OC_2H_5$, 45·2%. $C_{22}H_{24}O_6$ requires: C, 68·7; H, 6·3; $-OC_2H_5$ (4), 46·9%. Mixed m.ps. of this substance (VI B) with synthetic (VI A) described above and with triethyl dinatin separately were depressed (120–27° and 122–28° respectively).

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